

SOME SILYL ANIONS

BY

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EXPLANATION

The work included in this volume is partly by my own research, where indicated  
by asterisk. It has not been published, in whole or in part, by any other  
person, as far as I am aware of.

Wm. H. Jones

TO MY MOTHER

DECLARATION

The work included in this thesis is entirely my own except where otherwise stated. It has not been included, in whole or in part, for any other Degree, at this or any other University.

ACKNOWLEDGEMENTS

During the course of this work I have become indebted to many members, past and present, of the Chemistry Department. In particular I would like to thank my two supervisors Professor E.A.V. Ebsworth and Dr S. Craddock for their continued advice and enthusiasm.

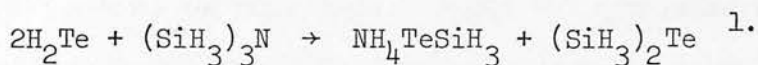
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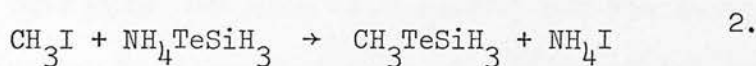


## SUMMARY

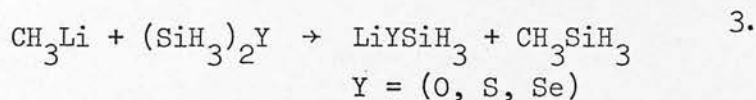
Two attempts to modify the ammonium salts of silyl thiol and silyl selenol were made in an effort to make them easily soluble. Both attempts were unsuccessful. The first was to try to form the potassium salt by using an ion exchange resin; the second was to prepare the methylsilyl derivative in the hope that it would be soluble. The ammonium salt of silyl tellurol was also prepared by an analogous route to the sulphur and selenium compounds.



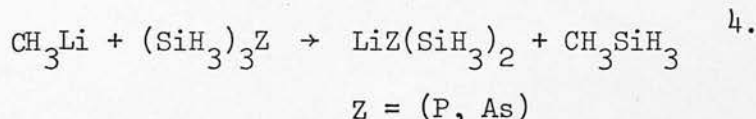
Methyl silyl telluride was prepared from it by adding methyl iodide.



Lithium silyl oxide, sulphide and selenide was prepared by the reaction of methyl lithium, as a solution in diethyl ether at  $-64^\circ$ , with disiloxane, disilyl sulphide and disilyl selenide.



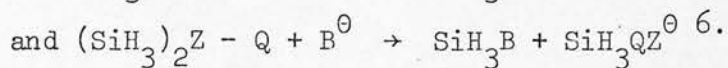
Similar reactions were carried out with methyl lithium and trisilyl phosphine and trisilyl arsine.



Yields of the lithium derivatives were all of the order of 80% and they were characterised by i.r., raman and n.m.r. spectroscopy. In some cases a reaction with trimethylsilyl chloride was also carried out.

Reactions of these compounds, as a solution in diethyl ether, were carried out with a variety of reagents but most were unsuccessful in that the desired products were not isolated. Instead, the main volatile silyl product was generally  $(\text{SiH}_3)_3\text{Z}$  or  $(\text{SiH}_3)_2\text{Y}$ . This

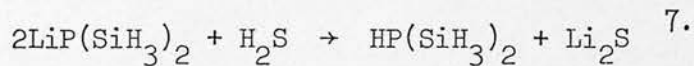
was attributed to the side-reactions:



where Q is any group of interest

and  $\text{B}^\ominus$  is a base - in this case  $\text{YSiH}_3$  or  $\text{Z}(\text{SiH}_3)_2$

This conclusion was confirmed by reactions of the silyl anions and closely related molecules producing exchange situations. Attempts to limit the extent of reactions (5) and (6) consisted of the use of benzene as a solvent, the use of trimethylamine and the absence of solvent. The first two were unsuccessful but the latter worked. It was possible to prepare disilyl phosphine and 1,1,1-trimethyl disiloxane by this method.



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Fig A2.1

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Fig A2.2

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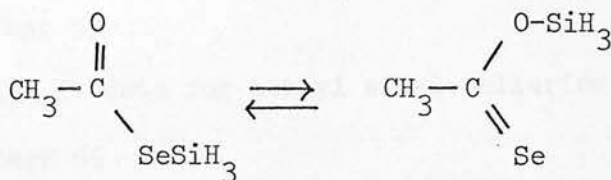


Fig A3.1

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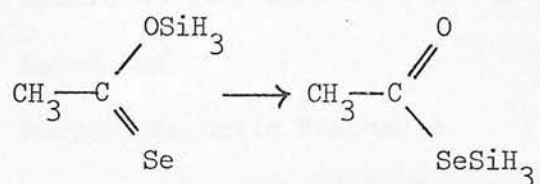


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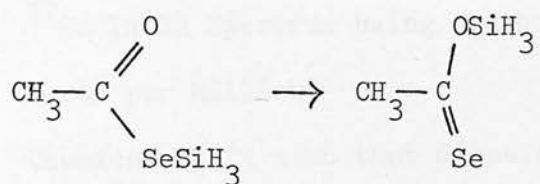


Table A2.7

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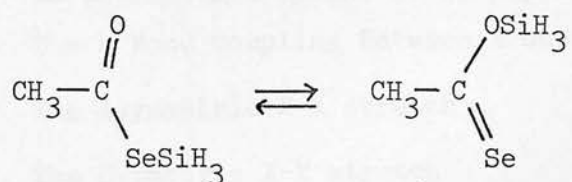


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Table A3.1 (b)

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Table A3.1 (c)

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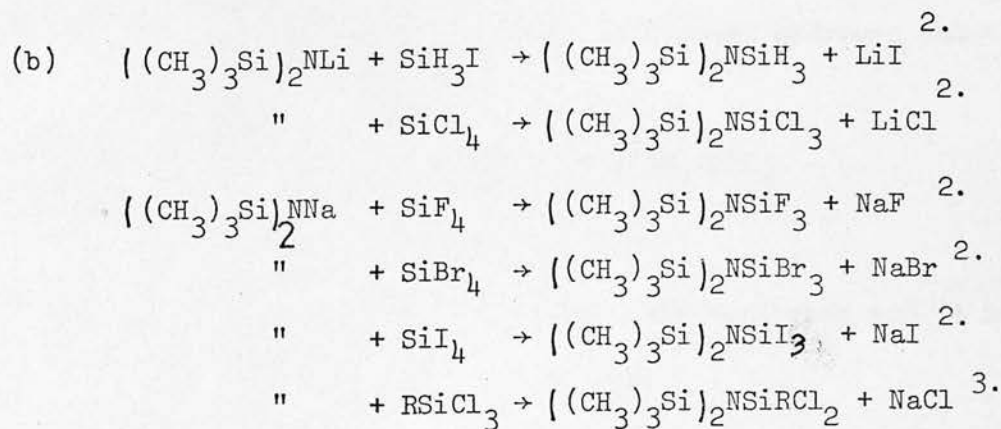
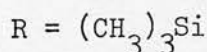
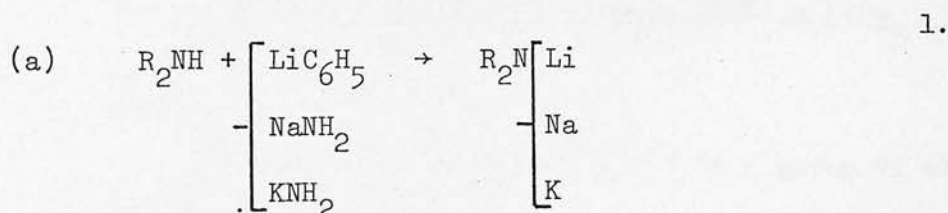
ABBREVIATIONS

H.N.S.D.	Hetero Nuclear Spin Decoupling
i.r.	Infra Red
n.m.r.	Nuclear Magnetic Resonance
$^1\text{H}$ -n.m.r.	Proton Nuclear Magnetic Resonance
$^{13}\text{C}$ -n.m.r.	Carbon Nuclear Magnetic Resonance
$^{19}\text{F}$ -n.m.r.	Fluorine Nuclear Magnetic Resonance
$^{31}\text{P}$ -n.m.r.	Phosphorous Nuclear Magnetic Resonance
$^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR	$^{29}\text{Si}$ INDOR Spectrum using Proton Signals
$^1\text{H}$ -( $^{31}\text{P}$ ) INDOR	$^{31}\text{P}$ INDOR Spectrum using Proton Signals
$^1\text{H}$ -( $^{77}\text{Se}$ ) INDOR	$^{77}\text{Se}$ INDOR Spectrum using Proton Signals
p.p.m.	Parts per Million
$\delta$	Chemical Shift such that Signals Downfield of the Reference are Positive and those Upfield Negative.
T	Proton Chemical Shifts such that Signals are relative to Tetramethyl Silane at 10 p.p.m.
$^n\text{J}(\text{X}-\text{Y})$	The n Bond Coupling Between X and Y.
$\nu_{\text{asym}}(\text{XY})$	The Asymmetric X-Y stretch
$\nu_{\text{sym}}(\text{XY})$	The Symmetric X-Y stretch
$\delta_{\text{asym}}$	An Asymmetric Deformation
$\delta_{\text{sym}}$	A Symmetric Deformation
$\rho$	A Rock
v.w.	very weak
w	weak
m	medium
s	strong
v.s.	very strong
sh	shoulder
n.o.	not observed
s	solvent band
o	Degrees Centigrade

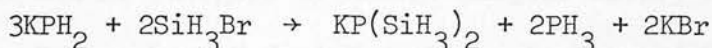
INTRODUCTION

In both Inorganic and Organic Chemistry one of the most successful types of synthesis involves the use of anionic species. One only has to consider the extensive preparative chemistry associated with Grignard and organo-lithium reagents to appreciate this point. It is not surprising to find that inorganic chemists, hoping to prepare silyl derivatives of Group V and VI, frequently attempt to prepare silyl anions of Group V and VI as potentially useful synthetic intermediates. Much work has been done in these fields, particularly with Group V organo-silyl derivatives, and so this account must of necessity be selective.

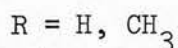
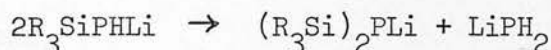
The use of organo-silyl amides as synthetic reagents is dominated by the work of Professor Wannagat and his co-workers. They have built up a large body of information concerning Si-N compounds in this way. The following reactions illustrate the approach used in the syntheses.



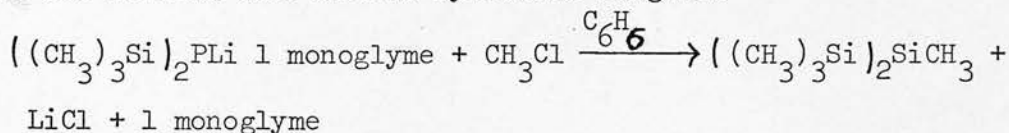
Although many derivatives of the type  $\text{MPR}_2$  ( $\text{M}$  = alkali metal) are known organo-silyl derivatives of this type have not been used to any great extent (see reference 4). The analogous silicon hydrides,  $\text{MP}(\text{SiH}_3)_2$ , have been prepared by the reaction of phosphinopotassium and silyl bromide<sup>5</sup>



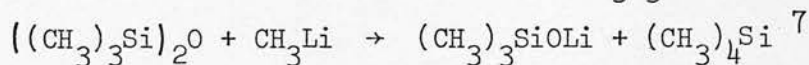
However, this route also leads to the formation of  $\text{KPH}(\text{SiH}_3)$ . The extent of the formation of the latter is difficult to control. Similar reactions occur with the analogous arsenic derivatives. Metallated disilyl phosphines have recently been prepared in mono-, di-, or triglyme by a rather circuitous route<sup>6</sup>.



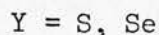
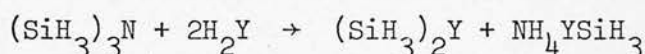
The metallated disilyl phosphines are isolated as etherates on evaporating the solvent and used as synthetic reagents



Few species of the type  $^{\text{O}}\text{Y SiR}_3$ , where  $\text{Y}$  is a group VI element, have been prepared. Lithium trimethylsilanolate,  $(\text{CH}_3)_3\text{SiOLi}$ , has been made



However it has not been used to any great extent for syntheses. The ammonium salts of silanethiol and silaneselenol,  $\text{NH}_4\text{SSiH}_3$  and  $\text{NH}_4\text{SeSiH}_3$ , have also been prepared by the reaction of trisilylamine and hydrogen sulphide or selenide.<sup>8</sup>



These derivatives have been used for some syntheses and it was their preparation that stimulated the present work.



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## CHAPTER 1

### Experimental Techniques and Preparation

#### of Starting Materials.



All manipulations of volatile compounds were carried out in a pyrex vacuum system of conventional design. High vacuum, necessary for the exclusion of air and moisture from the materials being handled, was maintained by means of a mercury diffusion pump backed by a rotary oil pump. Pressure inside the apparatus was measured using a Pirani gauge or (for pressures greater than ca. 1 mm) a spiral gauge, employed as a null point instrument with a lamp and scale (see figure 1.1).

The vacuum-line was built up from detachable sections. This aided cleaning, which was frequently necessary to remove involatile solid deposits which appeared in the system as decomposition products of the volatile species handled. Apiezon "L" and "N" greases were used on taps and ground glass joints. Much of the detachable apparatus used on the main semi-permanent system was fitted with "rotaflo" and "sovirel" teflon greaseless taps. These could withstand a pressure of several atmospheres if properly adjusted. A detachable trap section made up entirely from "sovirel" greaseless taps was also used when compounds of low volatility were being handled.

Certain convenient sections of high vacuum line were calibrated for volume using a molecular weight bulb. This enabled quantitative estimations of the amount of volatile materials present to be made rapidly from pressure readings. Compounds of low volatility were weighed in an ampoule fitted with a greaseless tap.

#### Criteria of purity

Generally a combination of the standard methods used in vacuum chemistry were employed to establish the nature and purity of a compound. Most impurities in a sample could be identified by some characteristic band in an i.r. vapour phase spectrum, which was often obtained as a

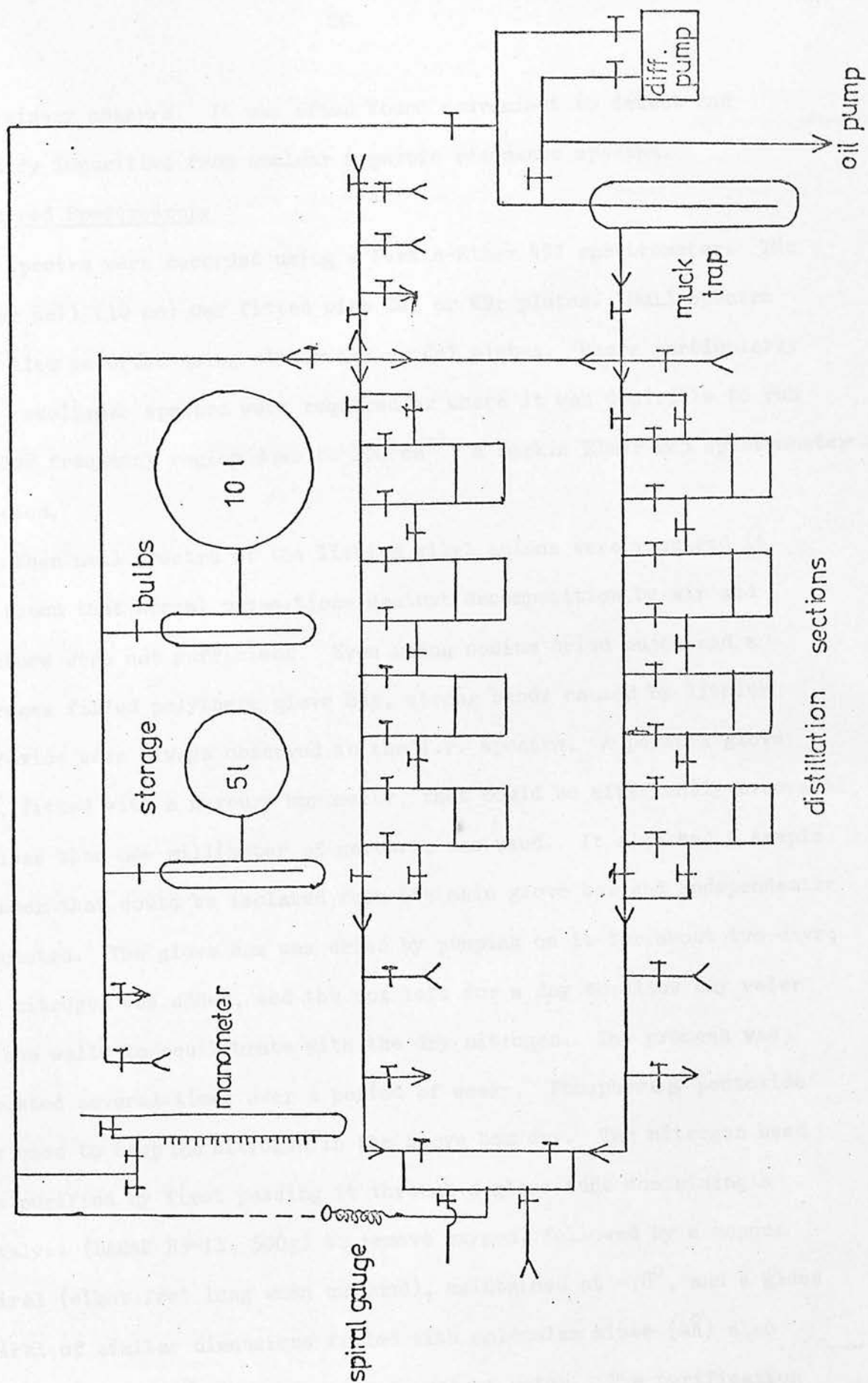


FIG. 1.1

preliminary measure. It was often found convenient to detect and identify impurities from nuclear magnetic resonance spectra.

### Infra-red Spectroscopy

I.r. spectra were recorded using a Perkin-Elmer 457 spectrometer. The vapour cell (10 cm) was fitted with CsI or KBr plates. Mull spectra were also recorded using either KBr or CsI plates. Where particularly high resolution spectra were required or where it was desirable to run the low frequency region down to  $200\text{ cm}^{-1}$ , a Perkin Elmer 225 spectrometer was used.

When mull spectra of the lithium silyl anions were required it was found that normal precautions against decomposition by air and moisture were not sufficient. Even using sodium dried nujol and a nitrogen filled polythene glove bag, strong bands caused by lithium hydroxide were always observed in the i.r. spectra. A perspex glove box, fitted with a mercury manometer, that could be efficiently evacuated to less than one millimeter of mercury, was used. It also had a sample chamber that could be isolated from the main glove box and independently evacuated. The glove box was dried by pumping on it for about two days; dry nitrogen was added, and the box left for a day to allow any water on the walls to equilibrate with the dry nitrogen. The process was repeated several times over a period of weeks. Phosphorus pentoxide was used to keep the nitrogen in the glove box dry. The nitrogen used was purified by first passing it through a glass tube containing a catalyst (BASAF R3-11, 500g) to remove oxygen, followed by a copper spiral (eight feet long when unwound), maintained at  $-78^{\circ}$ , and a glass spiral of similar dimensions filled with molecular sieve ( $4\text{\AA}$ ) also maintained at  $-78^{\circ}$ , to remove any traces of water. The purification apparatus was usually flushed out for several hours before attaching

it to the glove box or cooling the spirals. When filling the glove box the nitrogen was added over a period of about two hours.

Before mulls were made the small amount of fresh nitrogen required to fill the sample chamber was allowed to "dry out" for about twelve hours over phosphorus pentoxide. The nujol used was dried by heating it under vacuum with clean potassium until the potassium was just molten. It was maintained at this temperature for several hours. To remove any particles of potassium in the nujol it was filtered, under vacuum, through a glass sinter. After this treatment it was considered to be dry and left permanently in the glove box.

#### Raman Spectroscopy

Raman spectra were recorded using a Cary 83 Spectrometer using a blue laser (488 nm). When solution spectra of the silyl anions were required diethyl ether was used as the solvent since it was found to be a weak raman scatterer with no interfering bands.

#### Mass Spectroscopy

Mass spectra were reported on an A.E.I. M.S.9. spectrometer with an ionizing voltage of 70 eV., samples being bled in at very low pressures from a two litre bulb.

#### Nuclear Magnetic Resonance Spectroscopy

Proton n.m.r. spectra and INDOR spectra were recorded on a Varian Associates HA 100 spectrometer operating at 100MHz. This instrument was also fitted with a variable temperature control with a range of  $-100^{\circ}$  to  $+150^{\circ}$ .

Phosphorus n.m.r. spectra were recorded on a Varian Associates XL 100 spectrometer operating at 40 M.Hz. and in the Fourier transform mode. This instrument was also fitted with a variable temperature control.

In this work some use of the technique of INDOR (Internuclear Double Resonance) spectroscopy has been made. Since it is not a particularly common technique a short account of it follows:-

If a molecule contains two or more nuclei which have nuclear spins, then when observing one nucleus (usually  $^1\text{H}$ ) the others may also have an effect on the observed spectrum, and information about the n.m.r. spectra of the other nuclei can sometimes be obtained. For instance the  $^1\text{H}$ -n.m.r. spectrum of  $\text{SiH}_3\text{Q}$  (where Q is a non magnetic nucleus) consists of a main signal corresponding to  $^{28}\text{SiH}_3\text{Q}$  and a pair of satellites with a combined intensity 4.7% of the main resonance corresponding to  $^{29}\text{SiH}_3\text{Q}$  since the  $^{29}\text{Si}$  nucleus has a spin of  $\frac{1}{2}$  and a natural abundance of 4.7% ( $^{28}\text{Si}$  is non-magnetic). These are caused by coupling of the  $^{29}\text{Si}$  nucleus to the protons. It would obviously be of interest to be able to generate a  $^{29}\text{Si}$ -n.m.r. spectrum but direct observation of the  $^{29}\text{Si}$  nucleus presents formidable obstacles. For instance, the relative sensitivity of the  $^{29}\text{Si}$  nucleus at constant field for equal numbers of nuclei is 0.078 (with  $^1\text{H}$  at 1)<sup>1</sup>. However it is possible to generate a  $^{29}\text{Si}$ -n.m.r. spectrum from an  $^1\text{H}$ -n.m.r. spectrum using the INDOR technique which is really a slightly modified "tickling" or double resonance experiment. If the height of a  $^{29}\text{Si}$  satellite, in the  $^1\text{H}$ -n.m.r. spectrum of  $\text{SiH}_3\text{Q}$ , is monitored by an external recorder and an external frequency generator used to sweep through the  $^{29}\text{Si}$  frequency range at a constant rate, then as the  $^{29}\text{Si}$  frequencies of the molecule are reached the height of the  $^{29}\text{Si}$  satellite will vary corresponding to its partial collapse. Under favourable circumstances the ratios of the extent of collapse of the  $^{29}\text{Si}$  satellite would be



1:3:3:1 corresponding to one  $^{29}\text{Si}$  nucleus being split by three equivalent protons. The collapses of the satellite were monitored as a peak on the external recorder. Obviously they occur at intervals corresponding to  $^1J(^{29}\text{Si}-^1\text{H})$ . The  $^{29}\text{Si}$  frequency range was calculated using the relation:

$$X = \frac{100 \gamma(^{29}\text{Si})}{\gamma(^1\text{H})} \quad (1.1)$$

where X = frequency at which  $^{29}\text{Si}$  will resonate for protons at 100 MHz.

$$\begin{aligned} \gamma(^{29}\text{Si}) &= \text{magnetogyric ratio of } ^{29}\text{Si} \\ &= -5.314 \times 10^7 \text{ radians } \text{S}^{-1} \text{T}^{-1} \end{aligned}$$

$$\begin{aligned} \gamma(^1\text{H}) &= \text{magnetogyric ratio of } ^1\text{H} \\ &= 2.676 \times 10^8 \text{ radians } \text{S}^{-1} \text{T}^{-1} \end{aligned}$$

The external recorder used was a Smith's Servoscribe, which could be connected directly to the n.m.r. spectrometer signal output and calibrated in  $\text{Hz cm}^{-1}$  units. External frequencies were generated by a Schlumberger Frequency Synthesiser capable of being varied from 0 to 100 MHz. This synthesiser was connected to a constant velocity motor. Various scan speeds could be chosen by connecting it to various dials on the synthesiser. The power output of the synthesiser could also be varied as required (typically 0.1W was used).

Chemical shifts of the hetero-nuclei can also be obtained from the hetero-frequencies of the INDOR spectra. For purposes of comparison it is desirable to quote resonant frequencies obtained at some definite field strength and a convenient standard is that field in which T.M.S gives a proton resonance of exactly 100 MHz. Normally, the actual field used for the measurement will not correspond precisely to this frequency. In this case it can be corrected using the relation:

$$X = X_{\text{obs}} + X_{\text{obs}}(S - f + 100\delta)/10^8 \quad (1.2)$$

where  $X$  = required frequency

$X_{\text{obs}}$  = observed frequency in Hz

$S$  = frequency of the audio oscillator used to provide the locking signal

$f$  = the amount by which the actual centre band frequency of the spectrometer exceeds 100 MHz

$\delta$  = chemical shift to low field of T.M.S. of the signal used to actuate the field-frequency locking circuit. (in p.p.m.)

This equation applies when a low frequency sideband lock is used. The sign of  $S$  changes for a high frequency sideband lock. With this corrected frequency the hetero chemical shift can be calculated as usual using a known standard and the relation:

$$\delta = \frac{B_S - B_R}{B_R} \times 10^6 \quad (1.3)^1$$

where  $\delta$  = chemical shift

$B_S$  = field at which the sample resonates

$B_R$  = field at which the reference resonates

Note that  $\delta$  is positive for resonances to low field (high frequency) of the reference signal. The following example represents a typical calculation

Sample Lithium silyl selenide ( $\text{LiSeSiH}_3$ ) in diethyl ether at  $+28^\circ$

Experiment  $^{29}\text{Si}$  H.N.S.D. in the frequency sweep mode using the first upper side-band of diethyl ether as a lock (see fig. 3.7)

Observed average frequency = 19865536 Hz

=  $X_{\text{obs}}$

Actual frequency of the

spectrometer as measured by

the Schlumberger Synthesiser = 99,996,468 Hz

∴ correction required = -3532 Hz

= f

offset = 2500 Hz

= S

chemical shift of lock = +112 Hz relative to T.M.S.

= δ

Using relation 1.2

$$\begin{aligned} X &= 19865536 + 19865536 (-2500 + 3532 + 112)/10^8 \text{ Hz} \\ &= 19865536 + 227 \text{ Hz} \\ &= 19865763 \text{ Hz} \end{aligned}$$

Frequency of the  $^{29}\text{Si}$  nucleus of T.M.S. resonating under the conditions stated.

$$= 19867183 \text{ Hz}$$

∴ Using relation 1.3

$$\delta^{29}\text{Si} = \frac{(19865763 - 19867183)}{19.87} \text{ p.p.m.}$$

$$= -\frac{1420}{19.87} \text{ p.p.m.}$$

$$= -71.5 \text{ p.p.m.}$$

The technique outlined above can of course be extended to other nuclei. The convention used in this work is that if the n.m.r. spectrum of a nucleus, X, is generated using an  $^1\text{H}$  spectrum it is written as  $^1\text{H}-(\text{X})$ ;  $^1\text{H}-(^{29}\text{Si})$ ,  $^1\text{H}-(^{31}\text{P})$  and  $^1\text{H}-(^{77}\text{Se})$  spectra were recorded.

The chemical shift standards used are as follows:-



$^{29}\text{Si}$	frequency of $^{29}\text{Si}$ in T.M.S. = 19867183 Hz
$^{77}\text{Se}$	frequency of $^{77}\text{Se}$ in dimethyl selenide = 19071433 Hz
$^{31}\text{P}$	frequency of $^{31}\text{P}$ in ortho-phosphoric acid = 40480746 Hz
$^{125}\text{Te}$	frequency of dimethyl telluride = 3154971 Hz

All frequencies were corrected to the field in which T.M.S. gives a proton resonance at exactly 100 MHz. Chemical shifts to high frequency of the standards are positive.

INDOR spectroscopy can in favourable circumstances give information that would otherwise be exceedingly difficult to get. The main advantage of the technique is that it uses the very high proton sensitivity to generate spectra of nuclei with very low inherent sensitivities. The main disadvantage of the technique is that it can only really be easily applied to simple molecules since the observed INDOR spectra can be very misleading. The precise form of the spectra depend upon such factors as the amplitude of the irradiating field, the spacings in the irradiated spectrum and certain relaxation times.<sup>1</sup>

#### Handling of Materials

Vacuum-lines are really designed for the manipulation of air and moisture sensitive materials. Some of the techniques used to manipulate air and moisture sensitive solids are described below.

(a) Methyl lithium was obtained commercially as a molar solution in diethyl ether. Strictly speaking, this sample was a lithium halide

complex of methyl lithium, the presence of which had the effect of reducing the reactivity of the methyl lithium and making it stable to reaction with diethyl ether.<sup>2</sup> Although this solution was not pyrophoric it did form lithium hydroxide very rapidly when exposed to air. This impurity would almost certainly lead to the decomposition of silicon hydrides and so had to be rigorously excluded from the methyl lithium solution. Standardisation of the solution would also be more difficult in the presence of lithium hydroxide.

The apparatus used in the transfer of the methyl lithium to the reaction ampoule is shown on figure 1.2(a). The container was filled using standard techniques under dry nitrogen via tap (A). Using the calibrated section a known amount of methyl lithium solution could be measured out by closing tap (C) and cautiously opening tap (B). The reaction ampoule was filled with an atmosphere of diethyl ether, to minimise evaporation of diethyl ether from the methyl lithium solution, and with tap (B) closed tap (C) allowed the solution to run into the reaction ampoule. After a few minutes the solution in the reaction ampoule was cooled to  $-196^{\circ}$  and the constriction sealed off. The solution was degassed several times and was then ready for use. The main criterion of purity was that the solution was clear at room temperature and that no insoluble material was present since lithium hydroxide is insoluble in diethyl ether.

The procedure used for calibration of the solution was to hydrolyse the known volume of solution in the reaction ampoule with water. The lithium hydroxide formed was then titrated with standard acid. This was repeated at least three times. Using the technique methyl lithium could be delivered as a solution in diethyl ether to within an accuracy

of at least 0.05m moles and with no lithium hydroxide present.

(b) The lithium silyl anions were normally transferred as solutions in diethyl ether under an atmosphere of diethyl ether. It was important to exclude air and moisture. For instance, if an n.m.r. spectrum of a silyl anion was required, it was prepared in an ampoule fitted with a greaseless tap with an n.m.r. tube blown into the side of it. The ampoule could be removed from the vacuum line and the ether solution easily poured into the n.m.r. tube and then the tube sealed off as usual. Any volatile reagent could be easily distilled into the n.m.r. tube. Solid reagents presented more of a problem. Essentially it was a question of keeping the reactants cold enough to stop any reaction but still to allow transfer of the solution of the lithium anion. The procedure used was as follows:-

The same apparatus was used as before except that there was a greaseless tap between the n.m.r. tube and the ampoule. The insert of this tap was removed and the solid reactant added to the n.m.r. tube via the glass socket of the tap. The insert was then replaced and the apparatus pumped out. Methyl lithium was added to the main ampoule as before and the lithium silyl anion prepared in the main ampoule, in the normal way, with the connecting tap closed. This isolated the solid in the n.m.r. tube from any products of the anion preparation.

It was found possible to pour the resulting solution of the lithium silyl anion (at approximately room temperature) onto the solid in the n.m.r. tube, with the tube maintained at  $-78^{\circ}$ . Provided the transfer was made quickly enough this did not cause the diethyl ether to distill off the lithium silyl anion, probably as a consequence

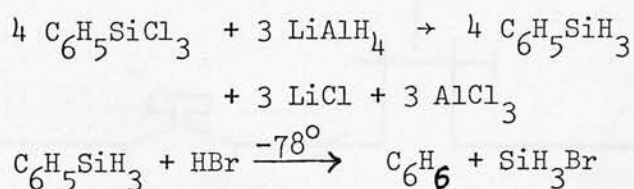
of the very small cross-sectional area of an n.m.r. tube. The tube could now be sealed off and warmed to higher temperatures in the n.m.r. spectrometer.

(c) Products from n.m.r. tubes could be easily transferred to the vacuum line for analysis using the apparatus shown on figure 1.2(b). The n.m.r. tube was weakened by scratching round the top with a glass knife. It was then inserted into tap (A) as shown and the apparatus pumped out. Diethyl ether (or the solvent in the n.m.r. tube) was distilled into the apparatus and allowed to reach its equilibrium vapour pressure. This prevented the solvent distilling off the solid. The n.m.r. tube could now be opened by cautiously turning tap (A) and the solution in the n.m.r. tube poured into tube (B), through the tap (A), and volatile materials could be distilled directly into the main vacuum line. Tube (B) was usually a fresh n.m.r. tube. This procedure was found to be quite successful and a surprisingly small amount of solid was lost in tap (A).

### Starting Materials

#### Silyl bromide

Silyl bromide was prepared by the method of Kummer and Fritz<sup>3</sup> on a 200m mole scale.



The reduction was carried out under dry nitrogen in di-n-amyl ether and purification of the silyl bromide achieved by distillation from  $-96^\circ$  into  $-120^\circ$ . It was identified by its i.r. spectrum.<sup>4</sup>

FIGURE 1.2(a)

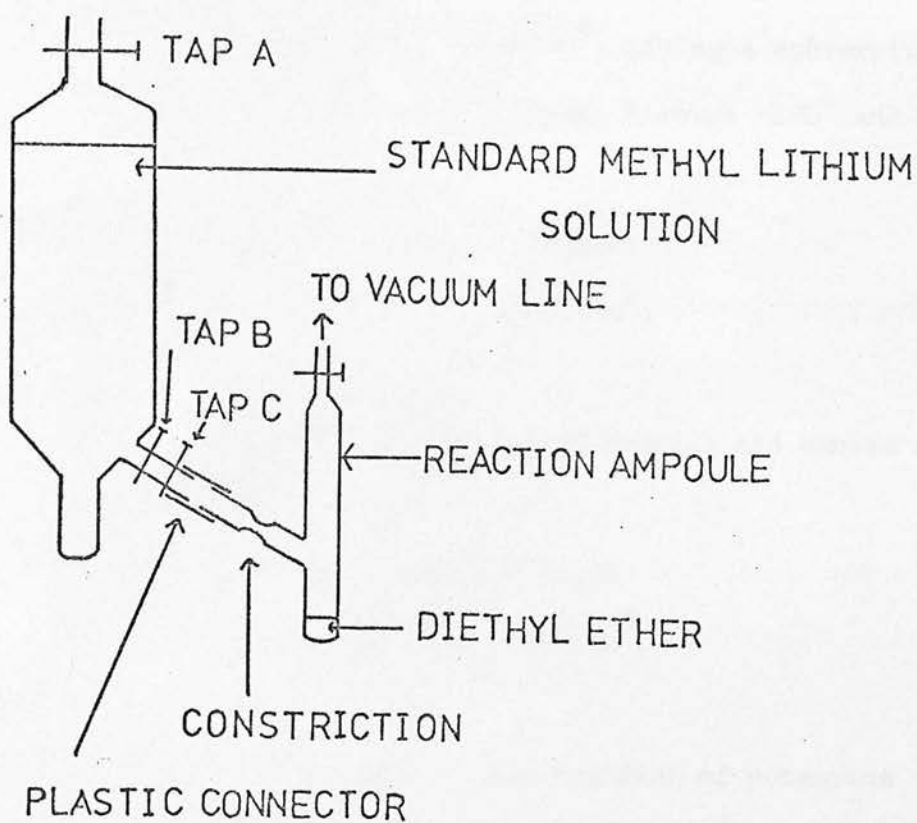
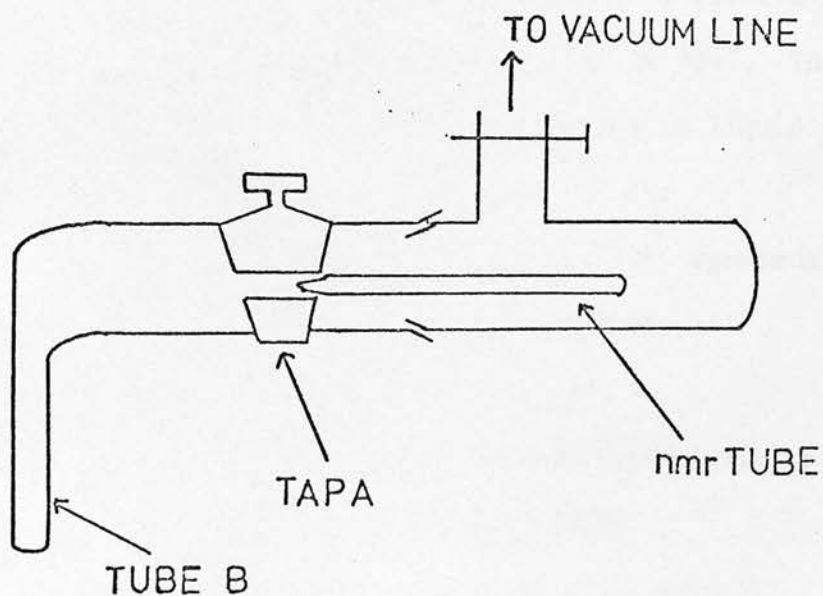


FIGURE 1.2 (b)





Silyl Chloride

Silyl chloride was prepared from silyl bromide by streaming it through an excess of dried mercuric chloride<sup>5</sup>, giving a conversion of about 95%. Separation was achieved by passage through  $-120^{\circ}$  and into  $-130^{\circ}$ .



The product was identified by its i.r. spectrum<sup>6</sup>.

Trisilylamine

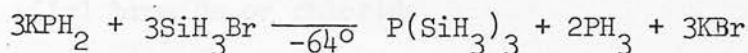
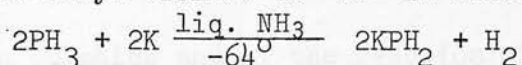
Trisilylamine was prepared by the reaction of ammonia and excess silyl chloride in the gas phase<sup>7</sup>.



The product was identified by its i.r. spectrum<sup>8</sup>.

Trisilylphosphine

Trisilylphosphine was prepared by the reaction of potassium phosphide and silyl bromide at  $-64^{\circ}$  in dimethyl ether<sup>9</sup>.



The purity was checked with an i.r. spectrum<sup>10</sup>.

Trisilylarsine

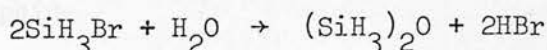
Trisilylarsine was prepared by the reaction between lithium arsenide and silyl bromide in dimethyl ether at  $-96^{\circ}$ . The lithium salt was formed by dissolution of the elements in liquid ammonia<sup>9</sup>.



The purity of the sample was checked by its i.r. spectrum<sup>9</sup>. This sample was kindly supplied by Dr R.A. Whiteford.

Disiloxane

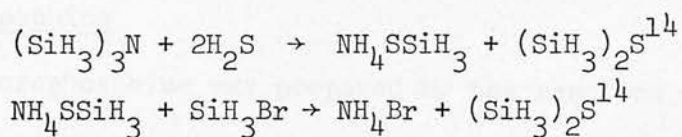
Disiloxane was prepared by the partial hydrolysis of silyl bromide<sup>11</sup>.



This was achieved by allowing water vapour to fill a small portion of the vacuum line, "squirting" silyl bromide into this section and allowing it to react for a few seconds. The sample was then passed through a  $-96^{\circ}$  bath to remove most of the water. The fractionation process was repeated several times. The hydrogen bromide produced dissolved in the water and any water present could be removed by repeating fractionation at  $-96^{\circ}$ . The yield of disiloxane was typically 85% but care had to be taken that the reaction time was only a few seconds otherwise hydrolysis of SiH bonds could occur and the yield of disiloxane could be low. This method was considered to be more convenient than the standard preparation which involves shaking ice-cold water and silyl iodide<sup>12</sup>. Purity was checked by its i.r. spectrum<sup>13</sup>.

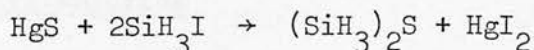
#### Disilyl Sulphide

Disilyl sulphide was prepared by the reaction of trisilylamine and hydrogen sulphide and by the reaction of ammonium silyl sulphide and silyl bromide or chloride.



Both reactions could be done in the same piece of apparatus. The overall yield of disilyl sulphide was typically 90%.

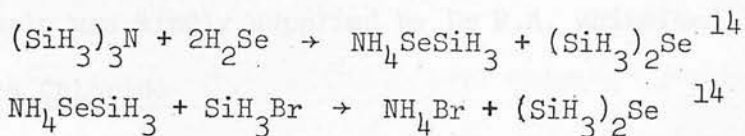
This method was considered to be more convenient than the standard one where mercuric sulphide reacts with silyl iodide<sup>14</sup>



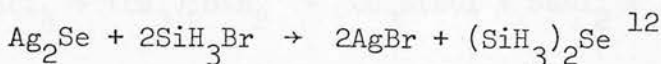
Purity was checked by its i.r. spectrum<sup>15</sup>.

#### Disilyl Selenide

Disilyl selenide was prepared in a completely analogous way to disilyl sulphide



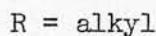
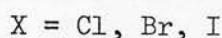
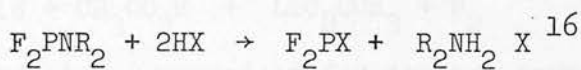
Again this method was considered to be more convenient than the standard silver selenide/silyl bromide preparation.



Purity was checked by its i.r. spectrum<sup>15</sup>.

#### Bromodifluorophosphine

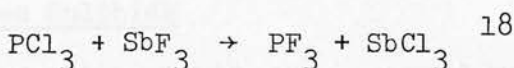
Bromodifluorophosphine was prepared by the general reaction of a hydrogen halide and a ( dialkylamino)difluorophosphine. In this case (dimethylamino)difluorophosphine was used.



The purity of the sample was checked by its i.r. spectrum<sup>17</sup> and kindly supplied by Mr D.E.J. Arnold.

#### Trifluorophosphine

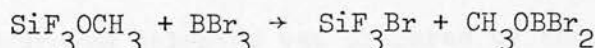
Trifluorophosphine was prepared by the reaction of phosphorus trichloride and antimony trichloride



The sample purity was checked by its i.r. spectrum<sup>19</sup> and the sample kindly supplied by Mr D.E.J. Arnold.

#### Trifluorosilyl Chloride

Trifluorosilyl chloride was prepared by the cleavage of trifluorosilyl methyl ether by boron tribromide.<sup>20</sup>



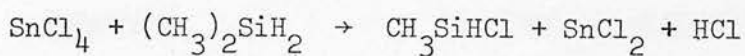
The purity of the sample was checked by its i.r. spectrum<sup>21</sup> and



the sample was kindly supplied by Dr R.A. Whiteford.

### Stannous Chloride

Stannous chloride was prepared in situ by the reaction of stannic chloride and dimethyl silane.<sup>22</sup>



The other products of the reaction were volatile and could be pumped off, leaving a pure sample of anhydrous stannous chloride.

### Lithium Acetate

Anhydrous lithium acetate was prepared by the reaction of lithium hydride and acetic acid in the absence of air.



The product was pumped on for several days to remove any traces of acetic acid.

### Trifluoroacetyl Bromide

Trifluoroacetyl bromide was prepared by the reaction of phosphorus pentabromide and perfluoroacetic anhydride.



The purity of the sample was checked by its i.r. spectrum.<sup>23</sup>

### Hydrogen Sulphide

Hydrogen sulphide was prepared by the reaction of ferrous sulphide and dilute hydrochloric acid.<sup>24</sup>



The product was dried by repeated fractionation at  $-96^\circ$  and identified by its i.r. spectrum.<sup>25</sup>

### Hydrogen Selenide

Hydrogen selenide was prepared by the reaction of freshly prepared aluminium selenide and dilute acid.

The following starting materials were obtained commercially. Samples used were of the highest purity available (at least 99%)

<u>Compound</u>	<u>Method of estimating purity</u>
Silicon tetrachloride	i.r. <sup>31</sup>
Methyl-trichlorosilane	i.r. <sup>32</sup>
Dichloro-dimethylsilane	i.r. <sup>32</sup>
Chloro-trimethylsilane	i.r. <sup>32</sup>
Methyl iodide	i.r. <sup>33</sup>
Acetyl chloride	i.r. <sup>34</sup>
Bromoacetyl bromide	i.r. <sup>35</sup>
Chloroacetyl chloride	i.r. <sup>35</sup>
Acetic anhydride	i.r. <sup>36</sup> and purified on a Fischer Spaltrohr-system distillation column to remove acetic acid.
Acetic acid	i.r. <sup>37</sup>
Perfluoroacetic anhydride	i.r. <sup>36</sup>
Perfluoroacetic acid	i.r. <sup>38</sup>
Carbon disulphide	i.r. <sup>39</sup>
Carbon dioxide (solid)	i.r. <sup>40</sup> and fractionation at -96° to remove any moisture.
Boron trichloride	i.r. <sup>41</sup>
Phosphorus pentabromide	-
Trimethylamine	i.r. <sup>33</sup>
Ammonia	i.r. <sup>42</sup> and stored over sodium.

### Solvents

The solvents used had to be rigorously dried and were of the highest purity commercially available. The following solvents were used and purified as follows:-

- (a). Ammonia - condensed several times onto sodium or potassium.
- (b) Benzene - stored on sodium wire.
- (c) Monoglyme - shaken with potassium and anthracene until the solution turned blue.
- (d) Dimethyl ether - distilled through  $-78^{\circ}$
- (e) Diethyl ether - stored on potassium.
- (f) Di-n-butyl ether - stored on lithium aluminium hydride.
- (g) Tetramethyl silane - stored on molecular sieve.
- (h) Tetrahydrofuran - passed through alumina (to remove peroxides) onto lithium aluminium hydride.

### Slush baths

Slush baths were made from a variety of solvents and either liquid nitrogen or solid carbon dioxide. Convenient temperatures were:-

- 160 $^{\circ}$  (isopentane/liquid nitrogen)
- 145 $^{\circ}$  (60/40 pet. ether/liquid nitrogen)
- 130 $^{\circ}$  (pentane/liquid nitrogen)
- 120 $^{\circ}$  (diethyl ether/liquid nitrogen)
- 112 $^{\circ}$  (carbon disulphide/liquid nitrogen)
- 96 $^{\circ}$  (toluene/liquid nitrogen)

- 78° (acetone/solid CO<sub>2</sub>)
- 64° (chloroform/liquid nitrogen)
- 45° (chlorobenzene/liquid nitrogen)
- 37° (dichloroethane/liquid nitrogen)
- 23° (carbon tetrachloride/liquid nitrogen)

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## CHAPTER 2

### THE ATTEMPTED MODIFICATIONS OF THE AMMONIUM

### SALTS OF Silyl THIOl AND Silyl SELENOL

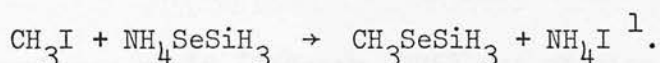
### AND

### THE PREPARATION OF AMMONIUM Silyl TELLURIDE

ATTEMPTED MODIFICATIONS OF THE AMMONIUM SALTS  
OF Silyl THIOl AND Silyl SELENOL

INTRODUCTION

The preparation of the ammonium salts of silyl thiol and selenol represent a potentially useful route to substituted silyl thio and silyl seleno derivatives. A small number of reactions have been carried out with these salts, e.g.



However, the salts were found to be insoluble in any of the solvents used. Reactions using these salts are therefore restricted to gas/solid and liquid/solid reactions. Furthermore, n.m.r. techniques cannot be used to follow reactions. It is obvious that modification of the salts to make them soluble would enhance their usefulness. Attempted modifications of the salts fall into two distinct lines of approach.

1. Modify the anion and retain the cation.
2. Modify or replace the ammonium cation and retain the anion.

The second approach is obviously preferable since it is the anion that is of interest. A possible alternative to the ammonium salt would be a tetra-alkyl ammonium salt. This would reduce any hydrogen bonding and also decrease the lattice energy of the salt by increasing the size of the cation. Both these effects would aid the solution of the salt. It should be noted that the N-methyl ammonium salts and N,N-dimethyl ammonium derivatives have been prepared and they too were insoluble in any of the solvents used<sup>1</sup>. Unfortunately, it is difficult to envisage a route to the tetra-alkyl ammonium salt which does not use the ammonium or N-methyl ammonium salts as an intermediate.

With the above points in mind an attempt to replace the ammonium ion by a potassium ion was made, using an ion exchange resin.

A second experiment was also carried out, in which the silyl thio group was converted into a methylsilyl thio group. It was hoped that the lattice energy of the salt would be reduced sufficiently to allow it to dissolve. These two experiments are described below.

### Experiment 2.1

#### The attempted preparation of potassium silyl sulphide from ammonium silyl sulphide

An ion-exchange resin (Zeocarb 225) was obtained in the acid form and converted to the potassium form by repeated washing with a saturated solution of potassium chloride. The resin was dried by washing it several times with potassium dried monoglyme and by adding molecular sieve ( $4\text{\AA}$ ) with each fresh portion of solvent. The resin was then pumped on for several days on a vacuum line and dry, degassed monoglyme distilled onto it.

Ammonium silyl sulphide (0.5 m mole) was prepared in an ampoule, fitted with a greaseless tap, and the ion-exchange resin in monoglyme was added to it under dry nitrogen. The ampoule was then left at room temperature for two days with vigorous periodic shaking.

Small quantities of silane ( $<0.1$  m mole) were detected by i.r. spectroscopy<sup>2</sup>. This was presumably caused by traces of water left on the resin. A solution i.r. spectrum of the monoglyme was run using cells that were capable of being sealed. They were filled under dry nitrogen and the sample beam was balanced for monoglyme by using an identical cell, filled with monoglyme, in the reference beam. No peaks were observed even though the amount of monoglyme used in the experiment had been kept to a minimum. Also, there was

no visible change in the crystals of the ammonium silyl sulphide in the ampoule.

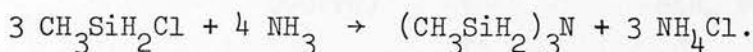
### Conclusion

This experiment was considered a failure because the ammonium silyl sulphide was not sufficiently soluble in monoglyme to allow "contact" between the resin and the salt.

### Experiment 2.2

The preparation of the ammonium salt of methylsilyl thiol and its attempted solution in benzene and monoglyme.

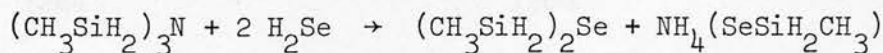
1,1',1''-trimethyl-trisilylamine was prepared in a completely analogous way to trisilylamine from methylsilyl chloride and ammonia.<sup>3</sup>



The product was identified by its i.r. spectrum.<sup>4</sup>

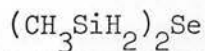
Hydrogen selenide (3m mole) was added to the 1,1',1''-trimethyl-trisilylamine (1m mole) in an ampoule fitted with a greaseless tap, and allowed to warm up to room temperature. The maximum pressure attainable was about one and a half atmospheres. Almost immediately small white crystals appeared and the reactants were left overnight.

The volatile products consisted of the excess hydrogen selenide which passed a  $-78^\circ$  slush bath and a compound (0.8m mole) which stopped at  $-78^\circ$ . It had an i.r. spectrum consistent with bis(methylsilyl) selenide (see table 2.1). The overall reaction was considered to be:



No attempt was made to identify the solid but by analogy with the preparation of ammonium silyl selenide its identity as the methylsilyl derivative was very likely. The yield, based on the amount of 1,1',1''-trimethyl-trisilylamine taken and the amount of bis(methylsilyl) selenide produced was 80%.

TABLE 2.1

I.r. spectrum of bis(methylsilyl) selenide

<u><math>\text{cm}^{-1} \pm 5</math></u>	<u>Assignment<sup>4</sup></u>
2970(w), 2910(vw)	$\nu$ CH
2150(s)	$\nu$ SiH
1410(w.Br.)	$\delta$ asy $\text{CH}_3$
1265(m)	$\delta$ sym $\text{CH}_3$
955(s)	$\text{SiH}_2$ bend
898(vs)	$\text{SiH}_2$ wag + $\rho$ $\text{CH}_3$
890, 885(vs) 870(sh)	
735(m)	$\nu$ Si-C + $\text{SiH}_2$ twist
490(w.Br.)	$\rho$ $\text{SiH}_2$
390	$\nu$ Si-Se

<u><math>(\text{CH}_3\text{SiH}_2)_2\text{O}</math></u>	<u><math>(\text{CH}_3\text{SiH}_2)_2\text{S}</math></u>	<u>Assignment<sup>4</sup></u>
<u><math>\text{cm}^{-1}</math></u>	<u><math>\text{cm}^{-1}</math></u>	
2970, 2920	2970	$\nu$ CH
2158	2160	$\nu$ SiH
1418, 1375	1375	$\delta$ asy $\text{CH}_3$
1264	1260	$\delta$ sym $\text{CH}_3$
964	952	$\text{SiH}_2$ bend
915	878	$\text{SiH}_2$ wag
880	(?)	$\rho$ $\text{CH}_3$
763	740	$\nu$ Si-C
(?)670	(?)	$\text{SiH}_2$ twist
520	No data	$\rho$ $\text{SiH}_2$
1085	-	$\nu$ Si-X



Dry, degassed benzene was added to the white crystals of ammonium methylsilyl selenide and the solution i.r. recorded as in the previous experiment. No bands were observed. Monoglyme gave a similar result.

Proton n.m.r. spectra of the benzene and monoglyme "solutions" gave no resonances except those of the "solvent". There was no obvious visible sign of the crystals going into solution.

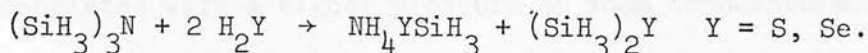
#### Conclusion.

Ammonium methylsilyl selenide can be prepared in high yield from 1,1',1''-trimethyl-trisilylamine and hydrogen selenide but it is not soluble in benzene or monoglyme.

## THE PREPARATION OF AMMONIUM SILYL TELLURIDE

### Introduction

It has been shown<sup>1</sup> that the ammonium salt of silyl thiol and silyl selenol can be prepared by the following route:-



By analogy, it should be possible to prepare the ammonium salt of silyl tellurol ( $\text{NH}_4\text{TeSiH}_3$ ).

Since tellurium compounds, and in particular hydrogen telluride, are frequently light-sensitive, all manipulations were carried out in a conventional vacuum-line covered in aluminium foil, to exclude light. It was found that hydrogen telluride decomposed to hydrogen and tellurium at moderate pressures. Tellurium appeared to facilitate the decomposition, and so frequent cleaning of the vacuum-line was necessary.

In a typical preparation of ammonium silyl telluride, hydrogen telluride (1 m mole) and trisilylamine (0.4m mole) were condensed into an ampoule fitted with a greaseless tap, with a volume of approximately fifty millilitres, and allowed to warm up to  $-23^\circ$ . After two hours, the volatile products were distilled out of the reaction ampoule and separated by trap to trap fractionation at  $-64^\circ$ . They consisted of disilyl telluride (0.068g, 0.35m moles) and the excess hydrogen telluride both were identified by their infrared spectra.<sup>5,6</sup> A very small amount of non-condensable gas was also produced. The reaction vessel was coated with a thin layer of a light grey, involatile, flaky solid (0.070g). These observations are consistent with the formation of ammonium silyl telluride.

In a similar reaction carried out at  $-78^\circ$ , no significant reaction had occurred after two days. When the reaction was carried out at

room temperature, only a trace of disilyl telluride was isolated. The volatile products consisted of trisilylamine identified by its i.r. spectrum<sup>7</sup> and a large amount of non-condensable gas, assumed to be hydrogen. The reaction ampoule was coated with a black solid, assumed to be tellurium. This is consistent with the decomposition of hydrogen telluride associated with a higher pressure at room temperature.

#### Identification of the solid

The solid formed in the above reaction was found to be insoluble in any common solvents, in particular potassium dried monoglyme (see reference 1). This excluded the use of nuclear magnetic resonance spectroscopy. Many attempts to make a mull of it in nujol and hexachlorobutadiene were all unsuccessful; so normal infrared spectroscopy could not be used. It was decided that in these circumstances the best method of identification was to attempt a simple chemical reaction. Methyl iodide was used as the reactant.

As in the previous reaction, trisilylamine (0.4m mole) and hydrogen telluride (1m mole) were allowed to react together at  $-23^{\circ}$ . Methyl iodide (0.4m mole) was added to the grey solid produced and allowed to react at room temperature for one hour. The volatile products were separated at  $-46^{\circ}$  by trap to trap fractionation. They consisted of methyl iodide, identified by its infrared spectrum, which passed  $-46^{\circ}$ , and a yellow liquid (0.3m mole) which stopped at  $-46^{\circ}$ . The infrared spectrum of this liquid (see table 2.2) was consistent with that expected for the new compound, methyl silyl telluride ( $\text{CH}_3\text{TeSiH}_3$ ). This assignment was confirmed by its mass spectrum which gave a parent peak corresponding to methyl silyl telluride.

mass required: 175.930139, for  $\text{CH}_3^{130}\text{Te}^{28}\text{SiH}_3$

mass found: 175.930278

error: < 2 p.p.m.

TABLE 2.2

I.r. spectrum of methyl silyl telluride

<u>Cm<sup>-1</sup> + 5</u>	<u>Assignment</u>
3020 v.w. ]	v CH
2940 m. ]	
2830 v.w. ]	
2150	v SiH
1235 m. ]	$\delta$ CH <sub>3</sub>
1225 m. ]	
1100 m.	Impurity of (SiH <sub>3</sub> ) <sub>2</sub> O
990 m.sh. ]	$\delta$ SiH <sub>3</sub> + $\rho$ CH <sub>3</sub> -Te
940 s.sh. ]	
875 v.s. ]	
755 w.	Impurity of (SiH <sub>3</sub> ) <sub>2</sub> O
555 m.	$\rho$ SiH <sub>3</sub> -Te + v C-Te *
n.o.	v Si-Te

\*\* Methyl Iodide<sup>8</sup>

<u>cm<sup>-1</sup></u>	<u>Assignment</u>
3050 w.	$\nu_4$ v CH
2950 s.	$\nu_1$
2841 w.	$2\nu_5$
2475 w.	$2\nu_2$
2118 w.	$\nu_2 + \nu_6$
1429 v.s.	$\nu_5$ $\delta$ CH <sub>3</sub>
1242 v.s.	$\nu_2$
887 v.s.	$\nu_6$ $\rho$ CH <sub>3</sub>
522 v.s.	$\nu_3$ v C-I

Disilyl Telluride<sup>5</sup>

<u>cm<sup>-1</sup></u>	<u>Assignment</u>
2188 v.s. ]	v SiH
2174 v.s. ]	
1118 v.w.	
955 w. ]	(SiH <sub>3</sub> ) <sub>2</sub> O
966 w. ]	
905 s.(b) ]	$\delta$ asy, $\delta$ sym SiH <sub>3</sub>
915 s.(b) ]	
864 s.(b) ]	
868 v.s.(a) ]	
875	

\* The value for  $\nu$  C-Te in (dimethyl telluride) is approximately  $530 \text{ cm}^{-1}$ .

\*\* Data for disilyl telluride and methyl iodide are included for comparison



This peak also had the very characteristic pattern of a mono-telluro compound.

It is interesting to note that the grey solid produced exactly the same reaction with methyl iodide after being exposed to light for one week at room temperature. Thus, it was considered stable to light.

The n.m.r. data obtained for methyl silyl telluride is listed in table 2.3. It is important to note that each of the singlets assigned to methyl silyl telluride has tellurium satellites caused by the isotope tellurium,  $^{125}\text{Te}$  which has a nuclear spin of one half and a natural abundance of seven percent. These satellites were shown to be due to tellurium by hetero nuclear spin decoupling (see introduction).

It is surprising that methyl silyl telluride does not show a resolved  $\text{H}-^{12}\text{C}-\text{Te}-^{28}\text{Si}-\text{H}$  coupling. This would produce two quartets as opposed to two singlets. With this in mind two experiments were done to attempt to detect any small coupling. The first involved irradiating the resonance at 9.78 p.p.m. and observing the effect on the resonance at 6.32 p.p.m. Under these conditions the resonance at 6.32 p.p.m. sharpened significantly, the peak width at half-height being reduced by fifty percent. This observation is consistent with there being an unresolved proton coupling between the two main resonances. The second experiment involved the phenomenon of "wobble-beats". This technique depends on the fact that if a single n.m.r. signal is traversed rapidly the main resonance is followed by a series of decaying oscillations. When there are two or more closely spaced signals, interference between the decay patterns produces "beats". The separation between beat maxima (measured in seconds) is equal to the reciprocal of  $J$ , where  $J$  is the separation of the main resonances (measured in hertz). Clearly, this simple relationship provides a method of measuring small values of  $J$ . Unfortunately, the n.m.r. spectrometer used was not really suited to this particular experiment. Figure 2.1 shows a typical



TABLE 2.3n.m.r. data for methylsilyl telluride

$$^1\text{SiH}_3 = 6.32 \pm 0.01 \text{ p.p.m.}$$

$$\text{CH}_3 = 8.78 \pm 0.01 \text{ p.p.m.}$$

$$^2\text{J}(^{125}\text{Te-Si-H}) = 14 \pm 0.2 \text{ Hz.}$$

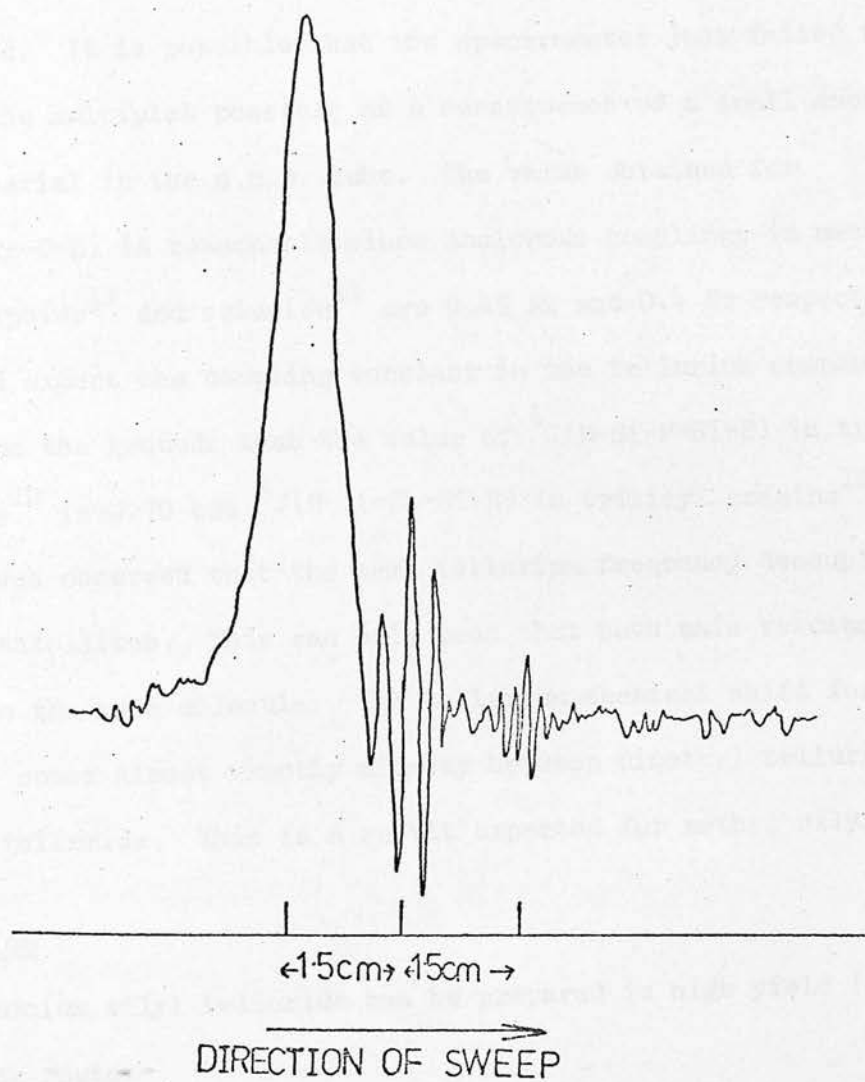
$$^2\text{J}(^{125}\text{Te-C-H}) = 11 \pm 0.2 \text{ Hz.}$$

$$^1\text{J}(^{29}\text{Si-H}) = 216 \pm 0.2 \text{ Hz.}$$

Average  $^{125}\text{Te}$  frequency to decouple satellites = 31528819 Hz. = -665 p.p.m.  
relative to dimethyl telluride

Note: Disilyl telluride is at -1340.7 p.p.m. (31507451 Hz), therefore  
methyl silyl telluride is almost exactly mid-way between  
dimethyl telluride and disilyl telluride as would be expected.<sup>10</sup>

FIGURE 2.1



SWEEP WIDTH = 50 HZ.

SCAN SPEED =  $0.5\text{cm. sec}^{-1}$

SEPARATION OF BEAT MAXIMA = 1.5cm.

= 3secs.

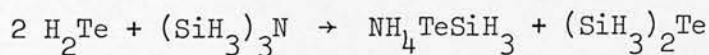
$\therefore J = 0.33\text{ HZ.}$

"wobble-beat" pattern. Analysis of these patterns yield a result for  $^4J(\text{H-C-Te-Si-H})$  of  $0.3 \pm 0.1$  hertz. It should be noted that the spectrometer should have been capable of resolving this coupling if the component lines were sharp. The fact that a "wobble-beat" pattern can be obtained indicates that the component lines are not very broad. It is possible that the spectrometer just failed to resolve the multiplet possibly as a consequence of a small amount of solid material in the n.m.r. tube. The value obtained for  $^4J(\text{H-Si-Te-C-H})$  is reasonable since analogous couplings in methyl silyl sulphide<sup>11</sup> and selenide<sup>11</sup> are 0.45 Hz and 0.4 Hz respectively. One would expect the coupling constant in the tellurium compound to be less on the grounds that the value of  $^4J(\text{H-Si-P-Si-H})$  in trisilyl-phosphine<sup>12</sup> is 0.70 but  $^4J(\text{H-Si-Sb-Si-H})$  in trisilyl stibine<sup>12</sup> is 0.57

It was observed that the same tellurium frequency decoupled both sets of satellites. This can only mean that both main resonances belong to the same molecule. The tellurium chemical shift for this molecule comes almost exactly mid-way between dimethyl telluride and disilyl telluride. This is a result expected for methyl silyl telluride.

### Conclusion

Ammonium silyl telluride can be prepared in high yield (80%) by the following route:-



It will also react with methyl iodide to give methyl silyl telluride in high yield (approximately 80%)



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### CHAPTER 3

PART A                    The preparation and characterisation of the  
lithium silyl anions of Group VI.

PART B                    The preparation and characterisation of the  
lithium disilyl anions of Group V.

PART C                    The stability of the silyl anions over a  
period of time.

## INTRODUCTION

For reasons outlined in Chapter 2 the use of the ammonium salts of silyl thiol, selenol and tellurol as synthetic reagents was discontinued in the hope that alternative routes to the formation of soluble analogues could be found. An alkali metal derivative was considered likely to be the most suitable; in particular the lithium derivative seemed particularly useful, since the Li-X bond tends to be partially covalent. This can lead to a milder reagent relative to the analogous sodium or potassium salts. The following experiments describe the preparation of the lithium silyl derivatives of Group VI and the lithium disilyl derivatives of Group V by the reaction of methyl lithium with the appropriate disilyl Group VI or trisilyl Group V derivative.

As is often the case in science this particular route came to light only as a result of an experiment that "failed" namely an attempt to remove the acidic hydrogen from silyl selenol by using methyl lithium.



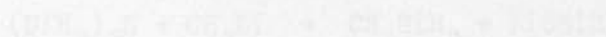
# The preparation and characterisation of lithium silyl anions

In a typical reaction, lithium (0.5 g, 0.045 mol) was added to a solution of dimethyl ether (10 ml) in a 100 ml round-bottomed flask equipped with a magnetic stirrer. The flask was cooled in an ice-water bath and the reaction mixture was stirred for 15 minutes. The mixture was then allowed to warm to room temperature and the stirring was continued for 1 hour. The mixture was then poured into a 250 ml beaker and the solid was dried in a vacuum oven at 50°C for 24 hours. The solid was then weighed (0.8 g, 0.045 mol) and the yield was 100%. The solid was a white powder and the melting point was 100°C.

## PART A

### PREPARATION AND CHARACTERISATION OF THE LITHIUM SILYL ANIONS OF GROUP VI.

The lithium silyl anions of Group VI were prepared by the reaction of lithium metal with dimethyl ether. The reaction was carried out in a 100 ml round-bottomed flask equipped with a magnetic stirrer. The flask was cooled in an ice-water bath and the reaction mixture was stirred for 15 minutes. The mixture was then allowed to warm to room temperature and the stirring was continued for 1 hour. The mixture was then poured into a 250 ml beaker and the solid was dried in a vacuum oven at 50°C for 24 hours. The solid was then weighed (0.8 g, 0.045 mol) and the yield was 100%. The solid was a white powder and the melting point was 100°C.



The yield of lithium silyl anions was 100% and the melting point was 100°C. The solid was a white powder and the melting point was 100°C. The solid was then weighed (0.8 g, 0.045 mol) and the yield was 100%. The solid was a white powder and the melting point was 100°C. The solid was then weighed (0.8 g, 0.045 mol) and the yield was 100%. The solid was a white powder and the melting point was 100°C. The solid was then weighed (0.8 g, 0.045 mol) and the yield was 100%. The solid was a white powder and the melting point was 100°C.

## Reaction 3.1

The preparation and characterisation of  
lithium silyl sulphide.

In a typical reaction methyl lithium (0.7m mole) as a molar solution in diethyl ether, was added to an ampoule fitted with a greaseless tap. Disilyl sulphide (1m mole) was distilled into the ampoule and the reaction allowed to take place at  $-64^{\circ}$  for thirty minutes. The volatile products were removed and fractionated by trap to trap distillation. They consisted of silane (0.1m mole) which passed  $-160^{\circ}$ , methyl silane (0.6m mole) which passed  $-120^{\circ}$  but stopped at  $-160^{\circ}$ , and the excess disilyl sulphide in diethyl ether. Products were identified by their i.r. spectra.<sup>1,2,3</sup> A small amount of hydrogen was detected but no methane. Unfortunately it was not possible to separate disilyl sulphide from diethyl ether and so the amount present could not be measured. The reaction also produced a white involatile solid, easily soluble in diethyl ether. This solid was considered to be a mixture of lithium silyl sulphide ( $\text{LiSSiH}_3$ ) and the lithium chloride initially present in the methyl lithium (see Chapter 1). The overall reaction was considered to be:

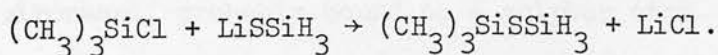


The yield of lithium silyl sulphide, based on the amount of methyl lithium used and the amount of methyl silane produced, was about 80%. The conditions given above represent the optimum conditions for the maximum formation of methyl silane. An excess of methyl lithium, for example, led to the formation of a larger proportion of silane and hydrogen.

Evidence for the formation of lithium silyl sulphide by the above reaction was afforded by the n.m.r., i.r. and Raman spectra of the solid and also by its reaction with trimethylsilyl chloride. It should be noted that elemental analysis of the solid could not be used to characterise lithium silyl sulphide because of the lithium halide present in the sample. Details of the evidence obtained are given below.

(a) Reaction with trimethylsilyl chloride.

Using disilyl sulphide (1m mole) and methyl lithium (0.7m mole) as before, a white solid was formed to remove any traces of disilyl sulphide, this solid was pumped on for several hours. Fresh diethyl ether (approximately 2 mls) was added. All the solid dissolved easily. Trimethylsilyl chloride (0.6m mole) was added and the reactants allowed to warm up to room temperature where upon a fast reaction took place forming a white precipitate, presumably lithium chloride. Analysis of the volatile products showed trimethylsilyl silyl sulphide (0.5m mole), identified by its characteristic i.r. spectrum<sup>4</sup>, was present. It was purified by trap to trap distillation at  $-46^{\circ}$ . A small amount of disilyl sulphide was also produced but it could not be measured since its isolation from diethyl ether was not possible. The overall reaction was considered to be:



The yield of trimethylsilyl silyl sulphide, based on the amount of trimethylsilyl chloride added was 80%.

Conclusion

The white solid produced by the reaction of methyl lithium and disilyl sulphide reacts with trimethylsilyl chloride as one would expect lithium silyl sulphide to.

(b) Nuclear magnetic resonance

The white solid was again prepared by the reaction of methyl lithium and disilyl sulphide. The  $^1\text{H}$ -n.m.r. spectrum of the solid using diethyl ether as a solvent was obtained by the method outlined in Chapter 1. The spectrum showed only one silyl compound to be present with its main signal at  $5.65 \pm 0.02$  p.p.m. and a  $^{29}\text{Si}$  satellite  $100 \pm 0.5$  Hz downfield. The other satellite was obscured by solvent signals (see fig 3.1). Thus  $^1\text{J}(^{29}\text{Si-H})$  was  $200 \pm 1$  Hz for this compound; in disilyl sulphide the chemical shift is 5.65 p.p.m. and  $^1\text{J}(^{29}\text{Si-H})$  is 224 Hz<sup>5,6</sup>.

A  $^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR spectrum was also recorded using the technique outlined in Chapter 1. This allowed an effective  $^{29}\text{Si}$  spectrum to be run using only proton signals. The spectrum obtained showed a quartet with signals in the ratio of 1:3:3:1 (see figure 3.2). It also yielded a value of  $^1\text{J}(^{29}\text{Si-H})$  of  $200 \pm 1$  Hz and  $\delta^{29}\text{Si}$  of  $-58 \pm 1$  p.p.m. for the compound; in disilyl sulphide  $\delta^{29}\text{Si}$  is  $-47 \pm 1$  p.p.m.<sup>7</sup> This spectrum shows that the white solid has three equivalent protons attached to one silicon atom.

Conclusion

The white solid produced by the reaction of methyl lithium and disilyl sulphide consists of a compound containing  $\text{SiH}_3$  groups in only one chemical environment, probably bound to a sulphur atom. Since the  $^{29}\text{Si}$  satellites are sharp singlets, only one  $\text{SiH}_3$  group can be bound to each sulphur atom.

(c) Infrared spectrum of the white solid

A solid phase i.r. spectrum of the material was also run using Nujol as a mulling agent. Details of the technique used are given in Chapter 1. The spectrum observed was very like that given by ammonium silyl sulphide<sup>4</sup>, as is shown in figure 3.3 and table 3.1

FIGURE 3.1

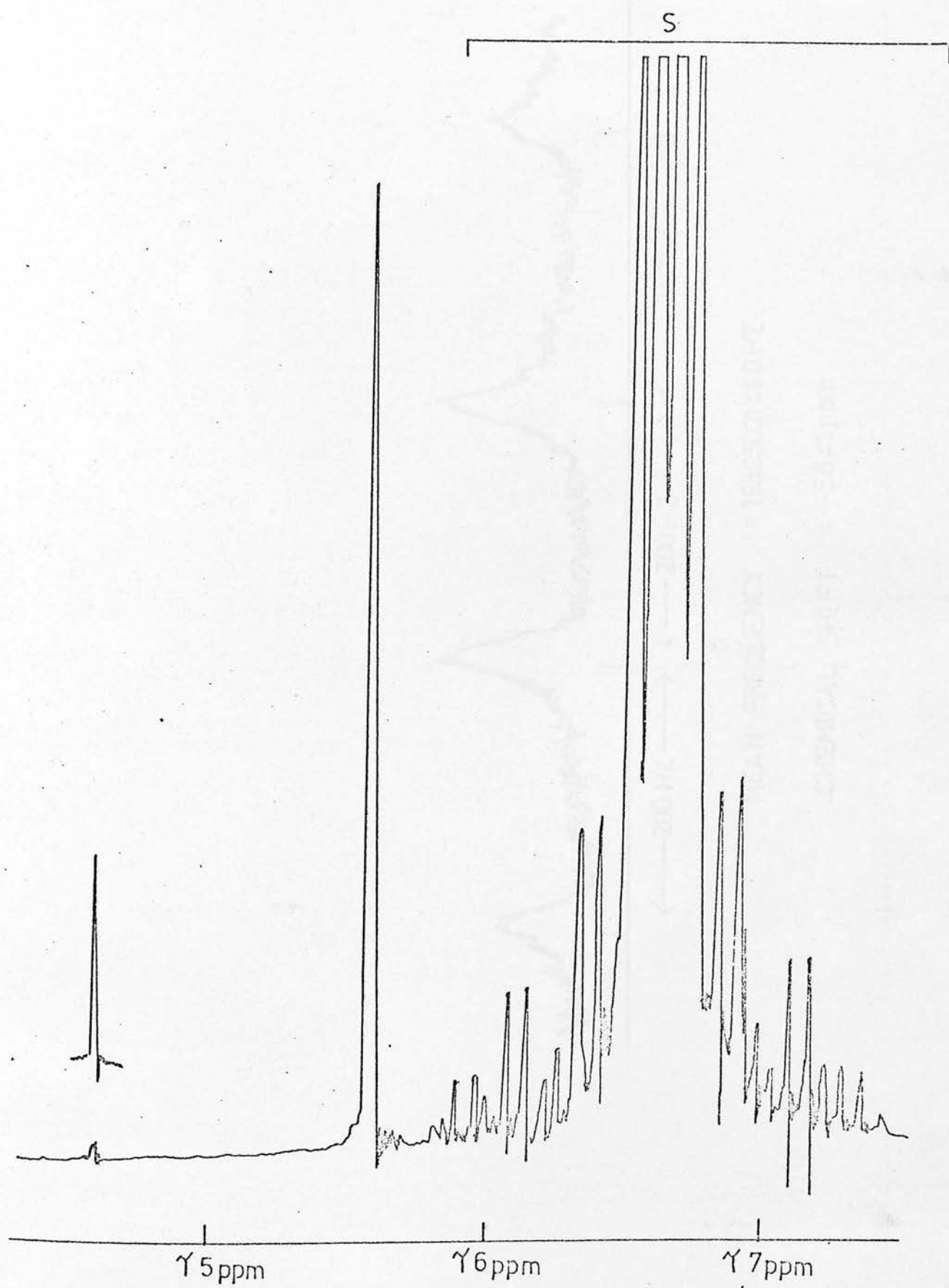
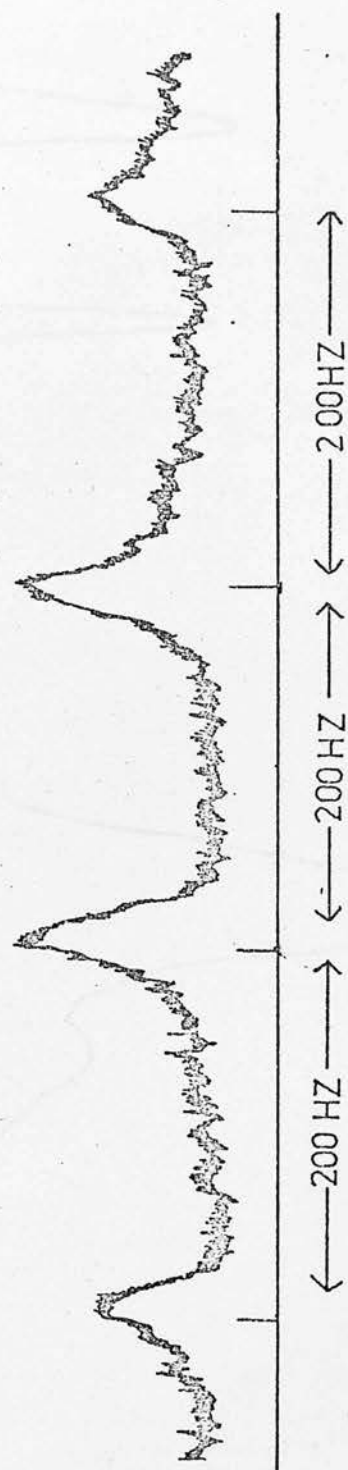


FIGURE 3.2



MEAN FREQUENCY =  $19866031 \pm 10$  HZ

CHEMICAL SHIFT =  $-58 \pm 1$  ppm



FIGURE 3.3

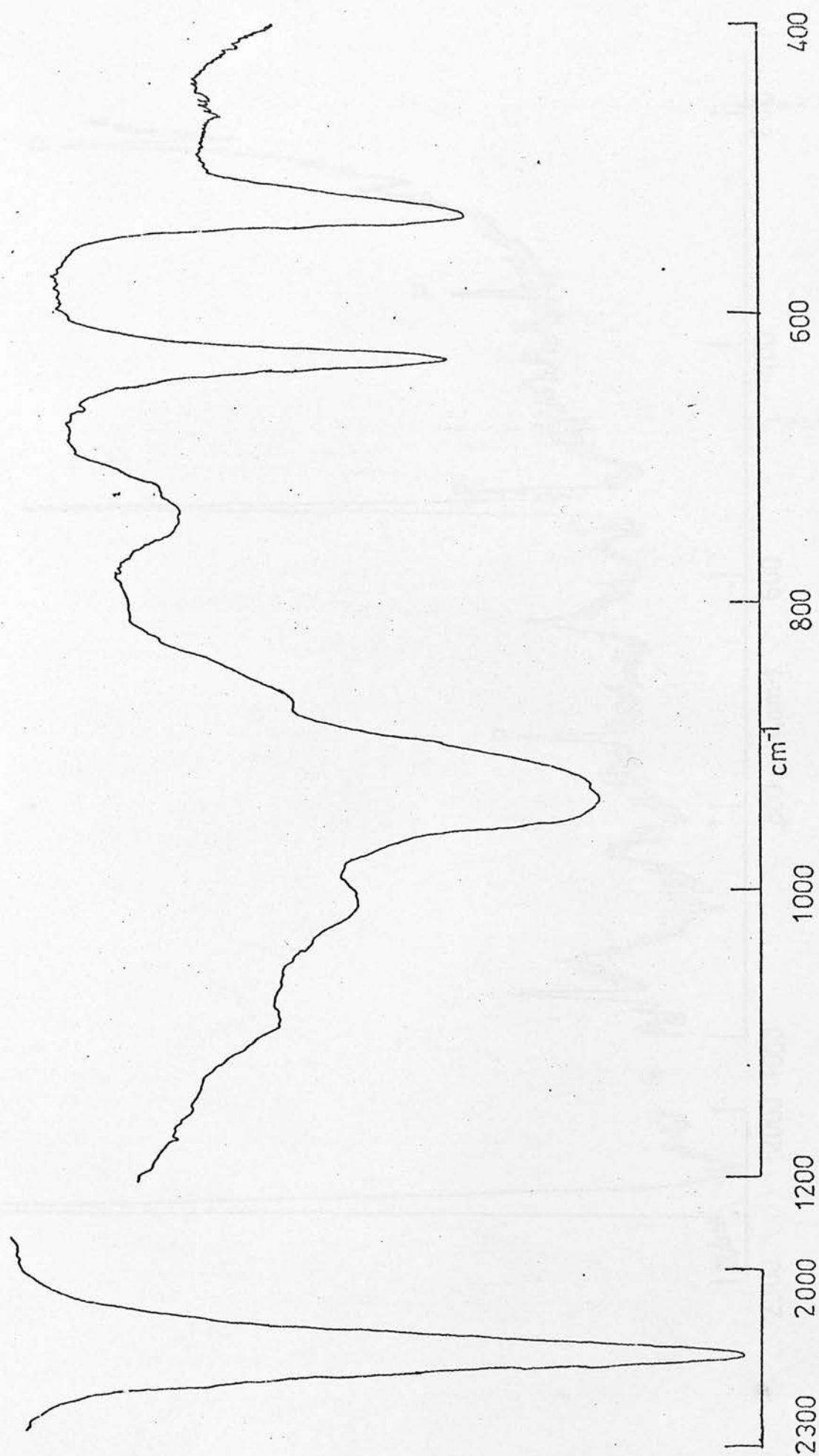


FIGURE 3.4

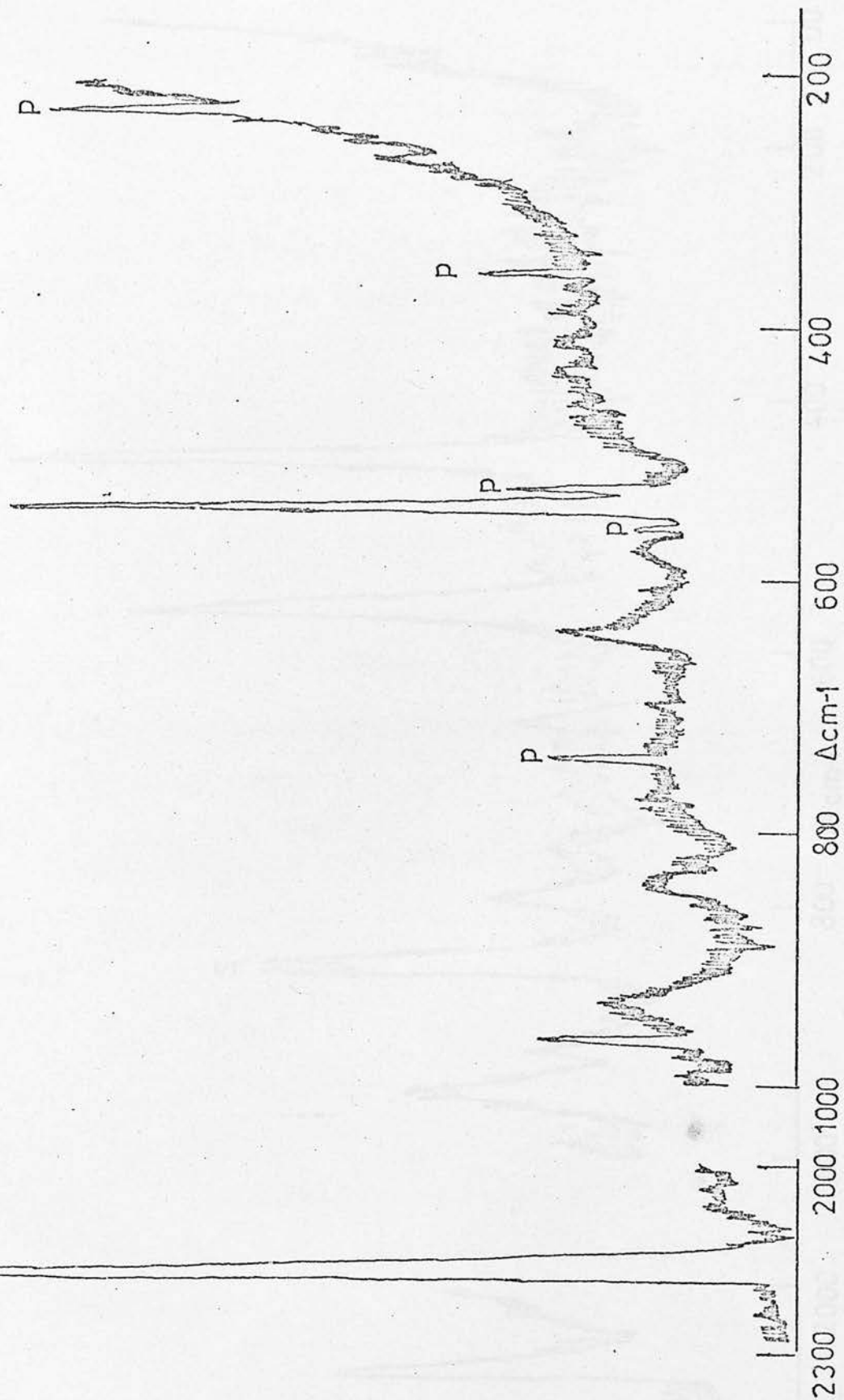


FIGURE 35

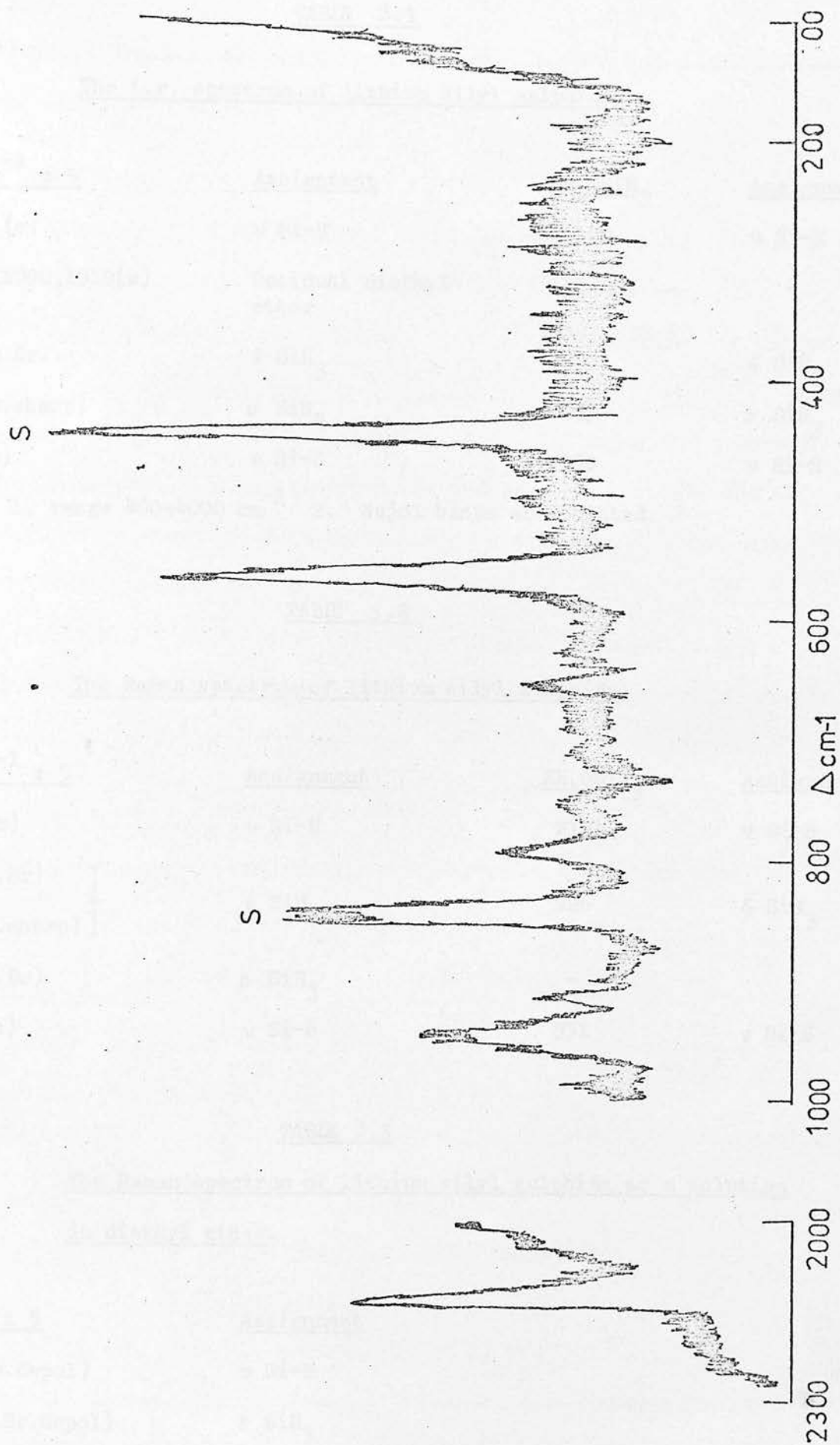


TABLE 3.1The i.r. spectrum of lithium silyl sulphide

$\text{cm}^{-1} \pm 5$	<u>Assignment</u>	$\text{NH}_4\text{SSiH}_3$	<u>Assignment</u> <sup>4</sup>
2145 (s)	v Si-H	2100	v Si-H
1250,1090,1010(w)	Residual diethyl ether	-	-
935(m.Br.)	$\delta \text{SiH}_3$	930	$\delta \text{SiH}_3$
630(m.sharp)	$\rho \text{SiH}_3$	635	$\rho \text{SiH}_3$
530(m)	v Si-S	550	v Si-S

Note 1. range 400-4000  $\text{cm}^{-1}$  2. Nujol bands are omitted.TABLE 3.2The Raman spectrum of lithium silyl sulphide

$\Delta \text{Cm}^{-1} \pm 5$	<u>Assignment</u>	$\text{NH}_4\text{SSiH}_3$	<u>Assignment</u> <sup>4</sup>
2165(m)	v Si-H	2124	v Si-H
964(m.Br) ]	$\delta \text{SiH}_3$	926	$\delta \text{SiH}_3$
935(m.sharp) ]			
640(w.Br)	$\rho \text{SiH}_3$	-	-
545(vs)	v Si-S	551	v Si-S

TABLE 3.3The Raman spectrum of lithium silyl sulphide as a solution in diethyl ether.

$\Delta \text{Cm}^{-1} \pm 5$	<u>Assignment</u>
2130(m.depol)	v Si-H
945(w.Br.depol)	$\delta \text{SiH}_3$
655 (v.w.Br., depol)	$\rho \text{SiH}_3$
565 (s.pol)	v Si-S

### Conclusion

The solid phase i.r. spectrum is consistent with the formulation of the material as lithium silyl sulphide.

#### (d) Raman spectra

A Raman spectrum of the white solid was obtained by the technique outlined in Chapter 1. The spectrum was very like that previously reported for ammonium silyl sulphide, as is shown on figure 3.4 and table 3.2<sup>4</sup>

A Raman spectrum was also obtained of a solution of the compound in diethyl ether. Again, the spectrum obtained was very like the solid phase spectrum of the ammonium salt.<sup>4</sup> (see fig. 3.5 and table 3.3) In addition, polarisation data could be obtained. In particular the band at  $565 \text{ cm}^{-1}$  assigned to  $\nu\text{Si-S}$  was strongly polarised as one would expect for the silyl-thio anion which belongs to the point group  $C_{3v}$ .

### Conclusion

As with the i.r. spectrum, the Raman spectra are consistent with the formulation of the white solid as lithium silyl sulphide.

### Overall Conclusion

The reaction of methyl lithium and excess disilyl sulphide produces lithium silyl sulphide in high yield.

### Reaction 3.2

#### The preparation and characterisation of lithium silyl selenide.

In a typical reaction methyl lithium (0.7m mole) as a molar solution in diethyl ether, was added to an ampoule fitted with a greaseless tap. Disilyl selenide (1 mole) was distilled into the ampoule and the

reaction allowed to take place at  $-64^{\circ}$  for thirty minutes. The volatile products detected and observations made were completely analogous to those in the previous experiment. The yield of methyl silane was 0.6m moles as before. The overall reaction was considered to be:



The yield of lithium silyl selenide ( $\text{LiSeSiH}_3$ ) based on the amount of methyl lithium used and the amount of methyl silane produced was 80%. The conditions given above represent the optimum conditions for the maximum formation of methyl silane. An excess of methyl lithium for example, led to the formation of a larger proportion of silane and hydrogen.

As in the previous experiment, evidence for the formation of lithium silyl selenide was afforded by n.m.r., i.r. and Raman spectroscopy and also by its reaction with trimethylsilyl chloride. As before, elemental analysis could not be used to characterise lithium silyl selenide. Details of the evidence are given below.

(a) Reaction with trimethylsilyl chloride.

Using disilyl selenide (1m mole) and methyl lithium (0.7m mole) as before, a white solid was formed. Diethyl ether was used as a solvent. Trimethylsilyl chloride (0.5m moles) was distilled into the reaction vessel. The reaction took place under exactly the same conditions as with lithium silyl sulphide. A white precipitate, presumably lithium chloride was formed rapidly and trimethylsilyl silyl selenide (0.5m mole), identified by its i.r. spectrum<sup>4</sup>, isolated from the reaction products by trap to trap distillation at  $-46^{\circ}$ . A small amount of disilyl selenide was also produced but it was not possible to isolate it from diethyl ether. The overall reaction was considered to be:



The yield of trimethylsilyl silyl selenide, based on the amount of



trimethylsilyl chloride added was 80%

### Conclusion

The white solid produced by the reaction of methyl lithium and excess disilyl selenide reacts with trimethylsilyl chloride as one would expect lithium silyl selenide to.

#### (b) Nuclear magnetic resonance

The white solid was again prepared by the reaction of methyl lithium and disilyl selenide. The  $^1\text{H}$ -n.m.r. spectrum of the solid, using diethyl ether as a solvent was obtained as before. The spectrum showed only one silyl compound to be present with its main signal at  $6.06 \pm 0.02$  p.p.m. and a  $^{29}\text{Si}$  satellite  $99 \pm 0.5$  Hz downfield. The other satellite was obscured by solvent signals (see figure 3.6) thus  $^1\text{J}(^{29}\text{Si-H})$  for this compound is  $198 \pm 1$  Hz; in disilyl selenide the chemical shift is 5.88 p.p.m.<sup>5</sup> and  $^1\text{J}(^{29}\text{Si-H})$  is 225 Hz<sup>6</sup>. Satellites of the main signal caused by the isotope of selenium,  $^{77}\text{Se}$ , which has a nuclear spin of one half and a natural abundance of 7.5%<sup>8</sup>, were also observed. The value of  $^2\text{J}(^{77}\text{Se}-^{28}\text{Si}-^1\text{H})$  was  $11 \pm 1$  Hz as compared to 15 Hz for disilyl selenide.<sup>9</sup> These satellites were only observed at temperature below about  $-20^\circ$ . The implications of these are discussed in Chapter 4.

An  $^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR spectrum was also recorded as before which showed a 1:3:3:1 quartet with a value of  $^1\text{J}(^{29}\text{Si-H})$  of  $199 \pm 1$  Hz (see figure 3.7). A value for  $\delta^{29}\text{Si}$  of  $-71 \pm 1$  p.p.m. was also determined as compared to a value of  $-58 \pm 1$  p.p.m.<sup>7</sup> for disilyl selenide.

An  $^1\text{H}$ -( $^{77}\text{Se}$ ) INDOR spectrum was recorded which also gave a quartet with signals in the approximate ratio of 1:3:3:1 (see figure 3.8) It should be noted that the baseline on this spectrum dips markedly on either side of the recorded signals. This may well be caused by an "off-resonance" effect but it does not detract from the validity of the

FIGURE 3.6

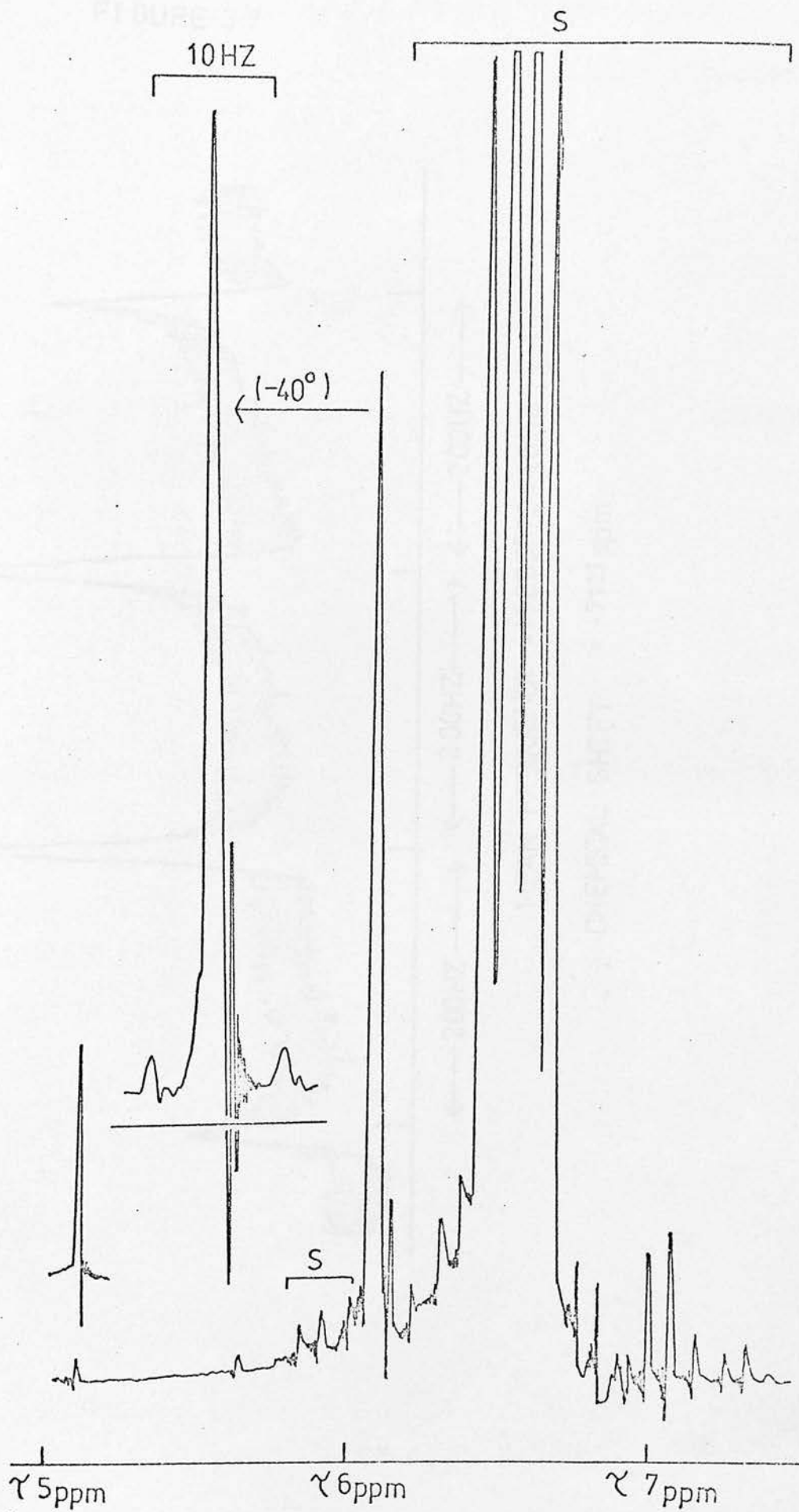


FIGURE 3.7

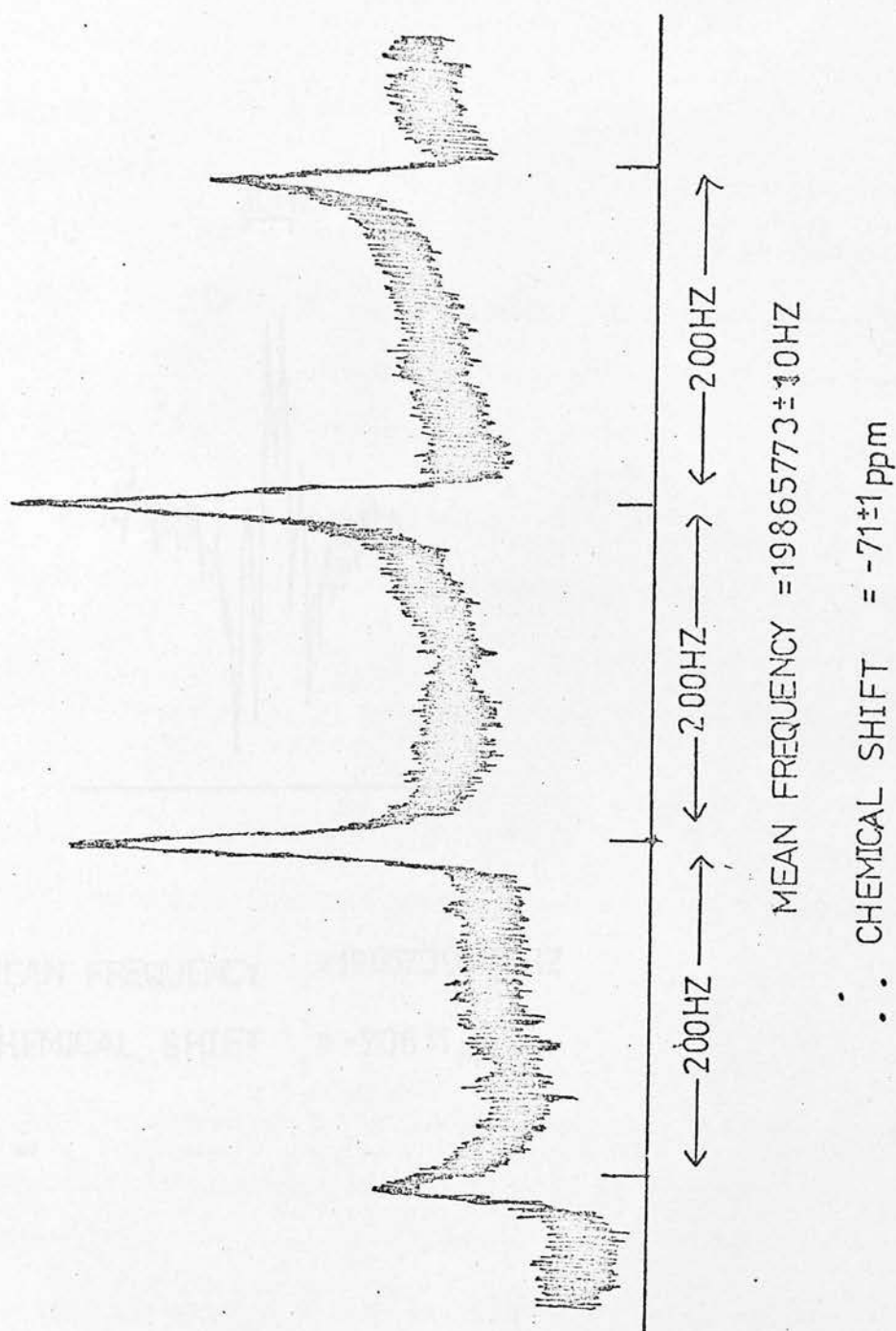
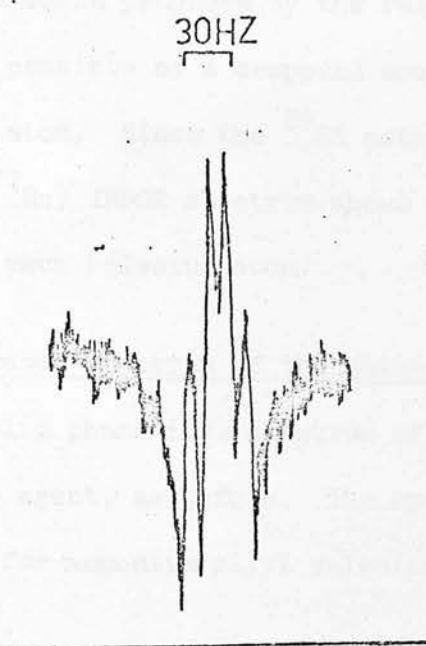


FIGURE 3.8



MEAN FREQUENCY =  $19057396 \pm 10 \text{ HZ}$

∴ CHEMICAL SHIFT =  $-736 \pm 1 \text{ ppm}$

spectrum obtained. The spectrum also gave a value of  $^2J(^1\text{H}-^{29}\text{Si}-^{77}\text{Se})$  of  $9 \pm 2$  Hz and  $\delta^{77}\text{Se}$  of  $-736 \pm 1$  p.p.m.; disilyl selenide has a value of  $-666 \pm 1$  p.p.m. for  $\delta^{77}\text{Se}$ .

#### Conclusion

The white solid produced by the reaction of methyl lithium and disilyl selenide consists of a compound containing  $\text{SiH}_3$  groups bound to a selenium atom. Since the  $^{29}\text{Si}$  satellites are sharp singlets and since the  $^1\text{H}-(^{77}\text{Se})$  INDOR spectrum shows a quartet only one  $\text{SiH}_3$  group can be bound to each selenium atom.

#### (c) Infrared spectrum of the white solid.

A solid phase i.r. spectrum of the solid was run using Nujol as a mulling agent, as before. The spectrum observed was very like that reported for ammonium silyl selenide,<sup>4</sup> as is shown on figure 3.9 and table 3.4.

#### Conclusion

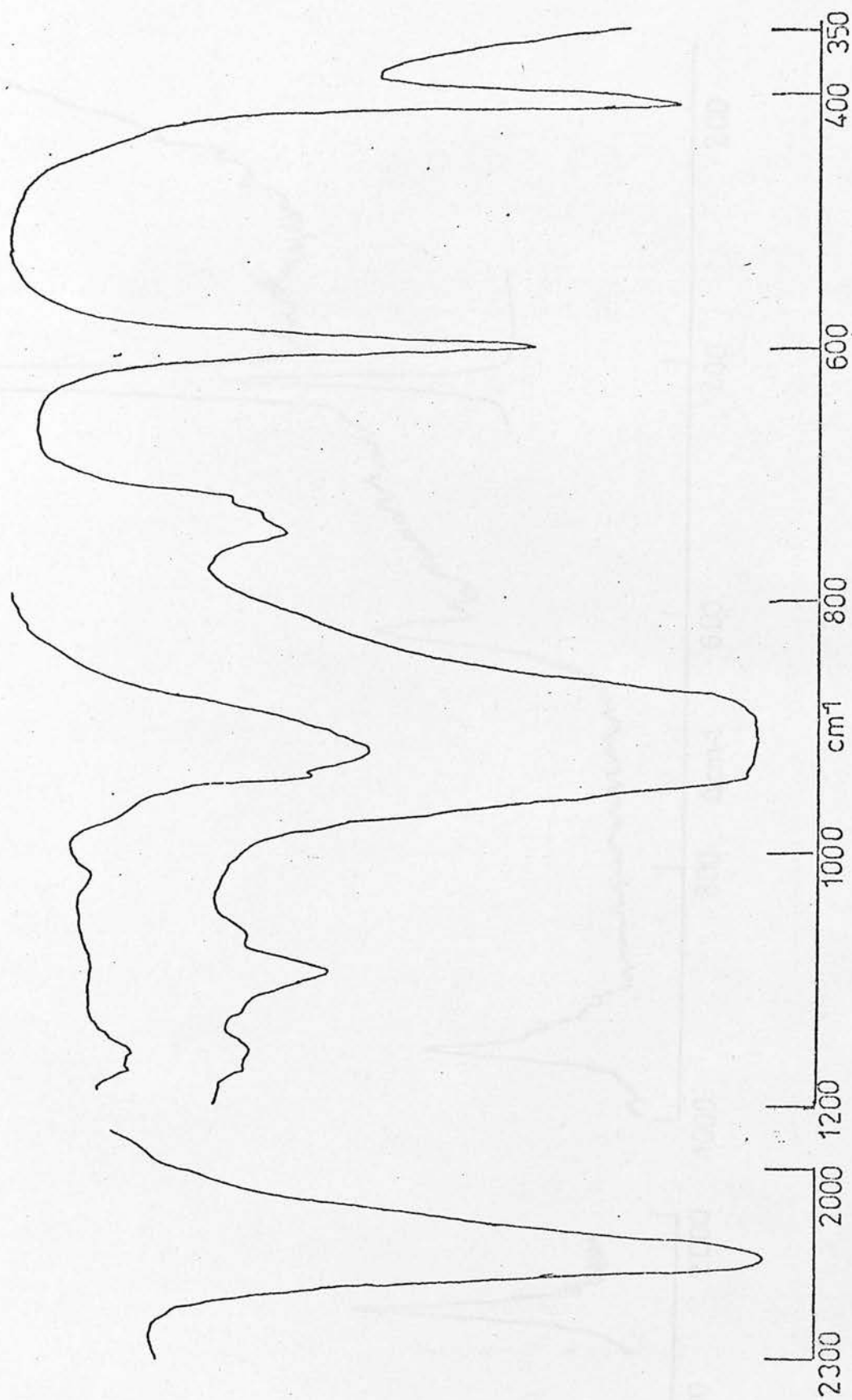
The solid phase i.r. spectrum is consistent with the formulation of the material as lithium silyl selenide.

#### (d) Raman spectra.

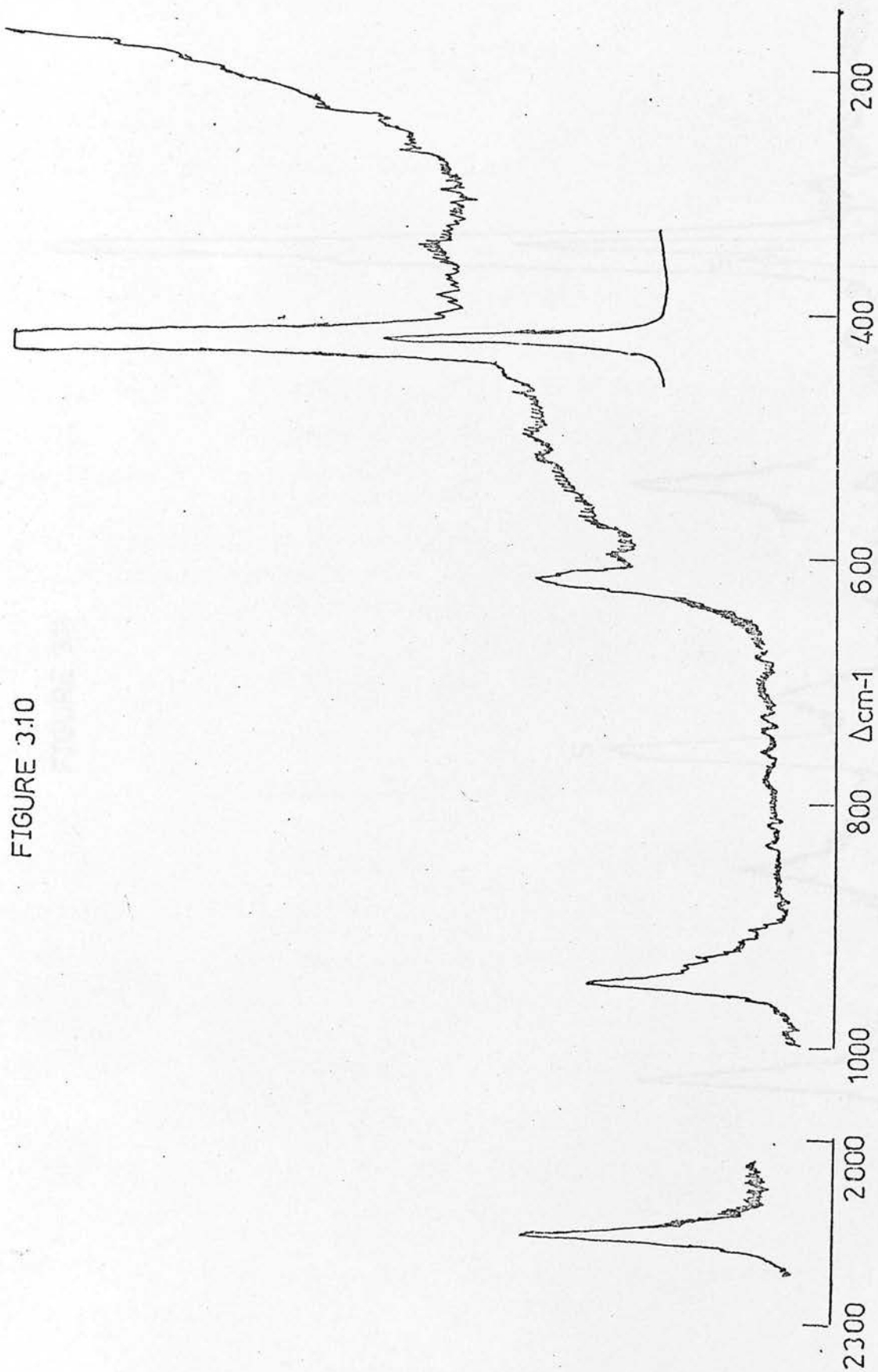
A Raman spectrum of the solid was obtained as before. The spectrum was very like that reported for ammonium silyl selenide.<sup>4</sup> (see figure 3.10 and table 3.5)

A Raman spectrum as a solution in diethyl ether was also obtained which was also like that of ammonium silyl selenide.<sup>4</sup> Polarisation experiments showed that the band at  $418 \text{ cm}^{-1}$ , assigned to  $\nu_{\text{Se-Si}}$ , was strongly polarised. This is what one would expect for the silyl selenide anion which belongs to the point group  $C_{3v}$ . (see figure 3.11 and table 3.6)

FIGURE 3.9







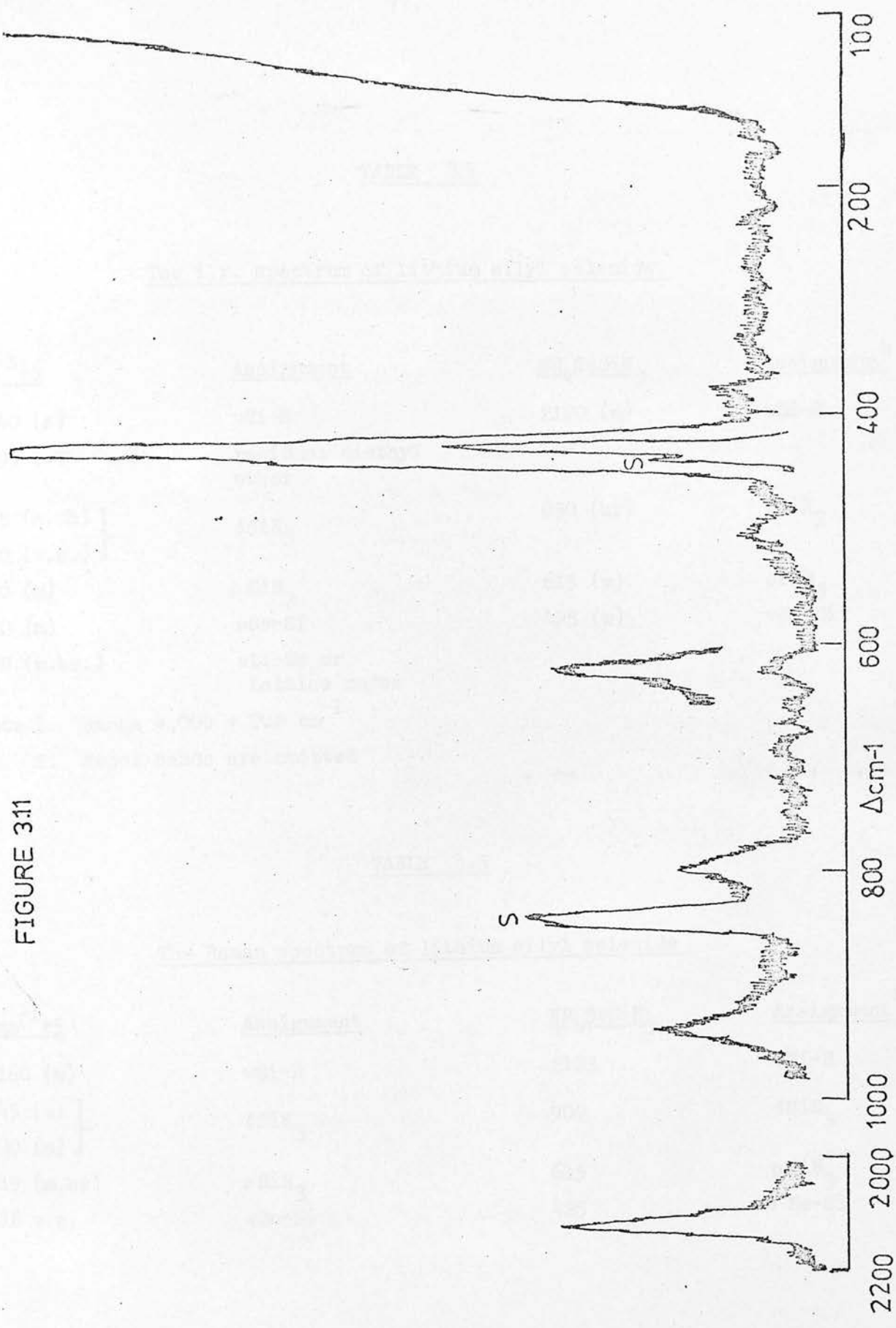


FIGURE 3:11

TABLE 3.4The i.r. spectrum of lithium silyl selenide.

<u>cm<sup>-1</sup> ± 5</u>	<u>Assignment</u>	<u>NH<sub>4</sub>SeSiH<sub>3</sub></u>	<u>Assignment<sup>4</sup></u>
2140 (s)	νSi-H	2120 (m)	νSi-H
1095 (w)	residual diethyl ether	-	-
945 (s.sh) ]	δSiH <sub>3</sub>	930 (br)	δSiH <sub>3</sub>
920 (v.s.) ]			
600 (m)	ρ SiH <sub>3</sub>	615 (m)	ρ SiH <sub>3</sub>
410 (m)	νSe-Si	425 (m)	νSe-Si
310 (m.br.)	νLi-Se or Lattice modes		

Note 1. Range 4,000 → 200 cm<sup>-1</sup>

2. Nujol bands are omitted

TABLE 3.5The Raman spectrum of lithium silyl selenide

<u>Δcm<sup>-1</sup> ± 5</u>	<u>Assignment</u>	<u>NH<sub>4</sub>SeSiH<sub>3</sub></u>	<u>Assignment<sup>4</sup></u>
2160 (m)	νSi-H	2123	νSi-H
945 (m) ]	δSiH <sub>3</sub>	900	δSiH <sub>3</sub>
930 (m) ]			
615 (m.br)	ρ SiH <sub>3</sub>	615	ρ SiH <sub>3</sub>
418 v.s.	νSe-Si	425	ν Se-Si

TABLE 3.6

The Raman spectrum of lithium silyl selenide  
as a solution in diethyl ether.

<u><math>\Delta\text{cm}^{-1} \pm 5</math></u>	<u>Assignment</u>
2118 (m., pol)	$\nu$ Si-H
940 (w.br., depol)	$\delta$ SiH <sub>3</sub>
624 (w.br., depol)	$\rho$ SiH <sub>3</sub>
429 (v.s. pol)	$\nu$ Se-Si

Note: Solvent bands are omitted.

### Conclusion

As with the i.r. spectrum, the Raman spectra are entirely consistent with the formulation of this compound as lithium silyl selenide.

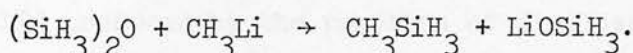
### Overall Conclusions

The reaction of methyl lithium and excess disilyl selenide produces lithium silyl selenide in high yield.

### Experiment 3.3

#### The preparation of characterisation of lithium silyl oxide.

In a typical reaction, methyl lithium (0.7m mole) as a molar solution in diethyl ether, was added to an ampoule fitted with a greaseless tap. Disiloxane (1m mole) was distilled into the ampoule and the reaction allowed to proceed at  $-64^{\circ}$  for thirty minutes. The volatile products detected were completely analogous to those in the two previous experiments. The yield of methyl silane (0.6m mole) was as before. The overall reaction was considered to be:



The yield of lithium silyl oxide ( $\text{LiOSiH}_3$ ), based on the amount of methyl lithium used and the amount of methyl silane produced was 80%. Again, the conditions used were the optimum ones for maximum production of methyl silane and hence lithium silyl oxide.

Evidence was afforded by n.m.r. and i.r. spectroscopy. As before, elemental analysis could not be used to characterise the lithium silyl anion. After several attempts at observing a Raman spectrum of this material it was concluded that lithium silyl oxide was an exceptionally bad scatterer and so it was not possible to obtain satisfactory Raman spectra. This behaviour is not uncommon

for small, oxygen containing molecules.<sup>10</sup> The reaction of lithium silyl oxide and trimethylsilyl chloride was not used since the reaction has complications which are described in Chapter 4.

Details of the evidence for the formation of lithium silyl oxide in the reaction of methyl lithium and disiloxane are given below.

(a) Nuclear magnetic resonance

An  $^1\text{H}$ -n.m.r. spectrum was obtained as before using diethyl ether as a solvent. The spectrum showed a main resonance at  $5.25 \pm 0.02$  p.p.m. with a sharp  $^{29}\text{Si}$  satellite  $97 \pm 0.5$  Hz downfield associated with it. The other satellite was obscured by solvent signals (see figure 3.12). Thus the value of  $^1\text{J}(^{29}\text{Si-H})$  is  $194 \pm 1$  Hz as compared to 5.39 p.p.m. for the chemical shift of disiloxane<sup>5</sup> and 221.5 Hz for the value of  $^1\text{J}(^{29}\text{Si-H})$ .<sup>6</sup>

An  $^1\text{H}$ -( $^{29}\text{Si}$ ) spectrum was also recorded. This showed a 1:3:3:1 quartet with  $^1\text{J}(^{29}\text{Si-H})$  equal to  $195 \pm 2$  Hz (see figure 3.13).  $\delta^{29}\text{Si}$  was  $-48 \pm$  p.p.m. as compared to disiloxane at  $-37.4$  p.p.m.<sup>7</sup>

Conclusion

The white solid produced by the reaction of disiloxane and methyl lithium consists of a compound containing  $\text{SiH}_3$  groups in only one chemical environment, probably bound to an oxygen atom.

(b) Infrared spectroscopy

A solid phase i.r. spectrum of the solid was obtained using Nujol as a mulling agent as before. The spectrum observed is shown on figure 3.14. The data obtained (see table 3.7) is consistent with the formulation of the material as lithium silyl oxide. Assignment of  $\nu\text{Si-O}$  was not certain especially in view of the residual ether bands that were present even after prolonged pumping on the solid. A possible solution would be to use isotopically labelled oxygen



FIGURE 3.12

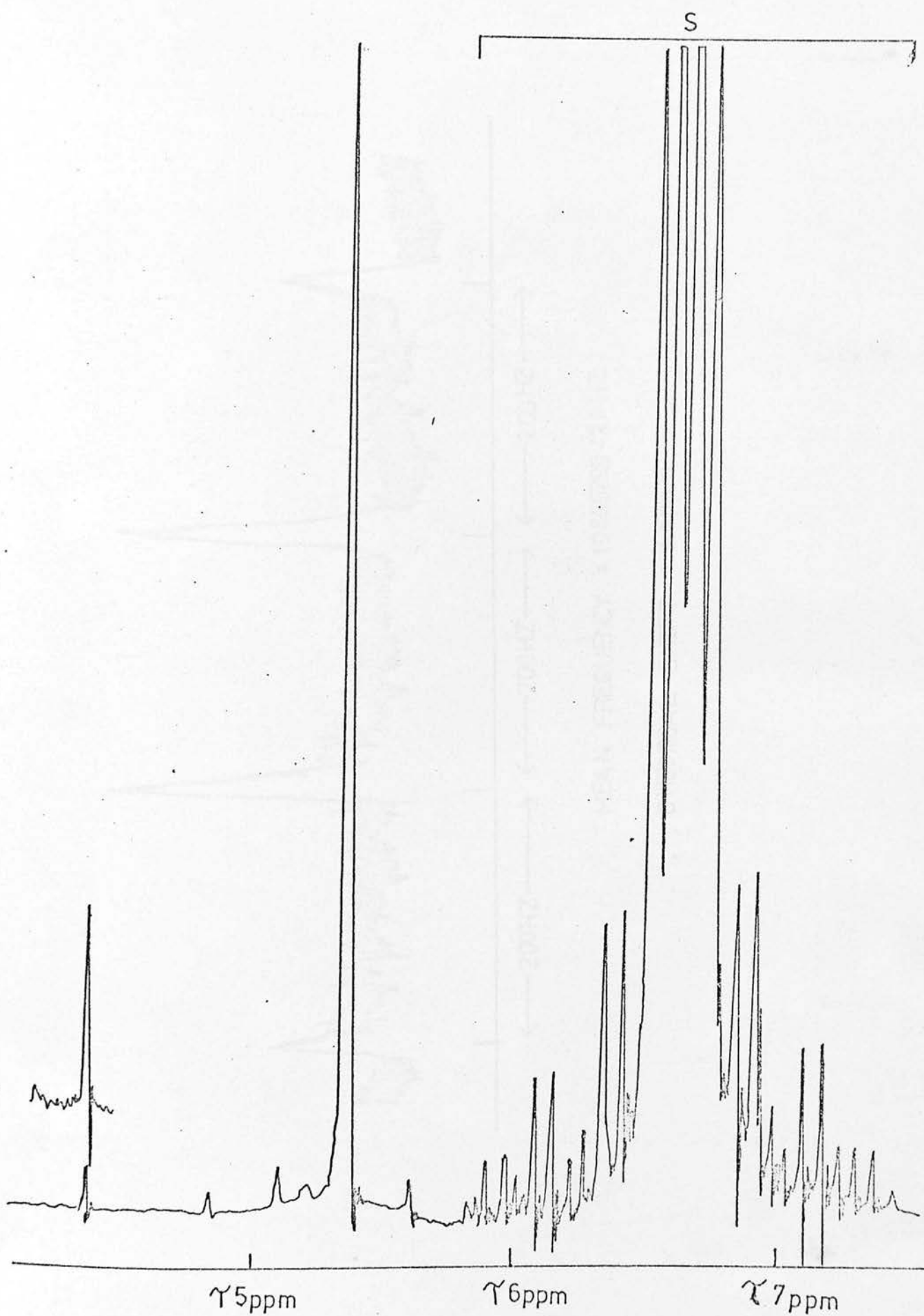


FIGURE 3.13

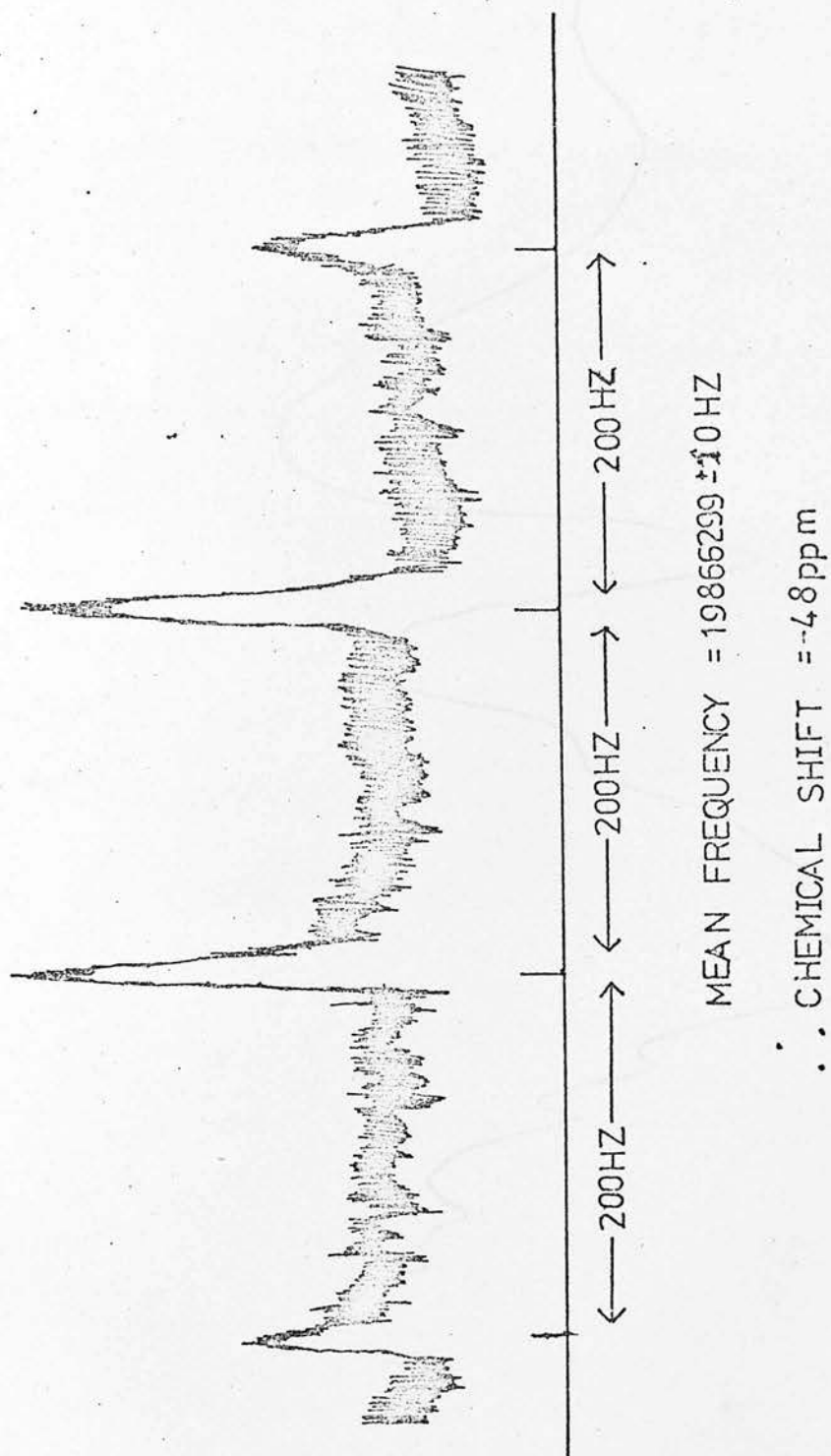


FIGURE 3.14

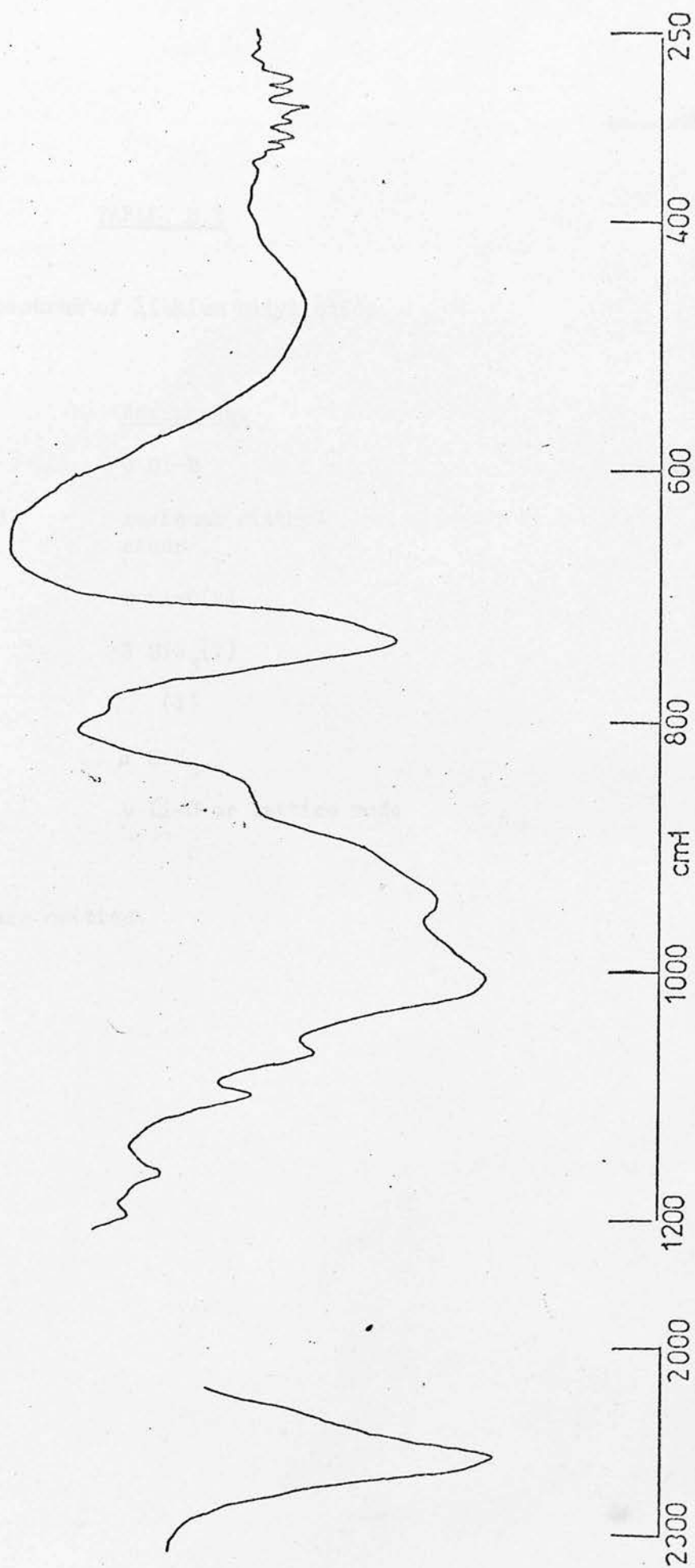


TABLE 3.7

The i.r. spectrum of lithium silyl oxide.

<u>cm<sup>-1</sup></u>	<u>Assignment</u>
2100 (s)	v Si-H
1190,1160,1095,1060	residual diethyl ether
1000 (s.br)	v Si-O(?)
940 (s.br)	$\delta$ SiH <sub>3</sub> (?)
850 (m.shoulder)	(?)
730 (s.br)	$\rho$ SiH <sub>3</sub>
465 (m.br)	v Li-O or lattice mode

Note Nujol bands are omitted.

and deuteration of the silyl group.

#### Conclusion

The i.r. spectrum is consistent with the formulation of the white solid as lithium silyl oxide.

#### Overall Conclusion

The reaction of methyl lithium and excess disiloxane produces lithium silyl oxide in high yield.

## PART B

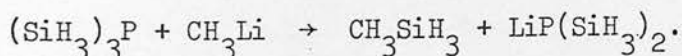
### PREPARATION AND CHARACTERISATION OF THE LITHIUM DISILYL ANIONS OF GROUP V



Experiment 3.4The preparation and characterisation of  
lithium disilyl phosphide.

In a typical reaction, methyl lithium (0.5m mole) as a molar solution in diethyl ether, was added to an ampoule fitted with a greaseless tap. Trisilylphosphine (0.7 mole) was distilled into the ampoule and the reaction allowed to take place at  $-64^{\circ}$  for thirty minutes. The volatile products were removed and fractionated by trap to trap distillation. They consisted of silane (0.05m mole) which passed  $-160^{\circ}$ , methyl silane (0.45 m mole) which passed  $-120^{\circ}$  but stopped at  $-160^{\circ}$ , and the excess trisilylphosphine (0.2m mole) which stopped at  $-78^{\circ}$ . Products were identified by their i.r. spectra<sup>1,2,11</sup>

A small amount of hydrogen was detected but no methane. The reaction produced a white solid, easily soluble in diethyl ether. This solid was considered to be a mixture of lithium disilyl phosphide and the lithium chloride initially present in the methyl lithium. The overall reaction was considered to be:



The yield of lithium disilyl phosphide ( $\text{LiP}(\text{SiH}_3)_2$ ), based on the amount of methyl silane produced was about 90%. The conditions given above represent the optimum conditions for formation of the maximum proportion of methyl silane. An excess of methyl lithium led to the formation of a larger proportion of silane and hydrogen.

Evidence for the formation of lithium disilyl phosphide by the above reaction was afforded by n.m.r., i.r. and Raman spectra of the solid. Details of the evidence are given below.

(a) Nuclear magnetic resonance.

The white solid was prepared by the reaction of methyl lithium and

trisilylphosphine as before. The  $^1\text{H}$ -n.m.r. spectrum of the solid was recorded using diethyl ether as a solvent. The spectrum showed only one silyl compound to be present with its main signal at  $6.02 \pm 0.02$  p.p.m., split by the  $^{31}\text{P}$  nucleus, into a doublet with  $^2J(^{31}\text{P}-^{28}\text{Si}-^1\text{H})$  equal to  $15.5 \pm 1$  Hz. In addition a  $^{29}\text{Si}$  satellite was observed  $92 \pm 0.5$  Hz downfield of the main signal, also split into a phosphorus doublet. The other satellite was obscured by solvent resonances (see figure 3.15). Thus the value of  $^1J(^{29}\text{Si}-\text{H})$  was  $184 \pm 1$  Hz. A long range coupling on each of the  $^{29}\text{Si}$  satellite components was also observed. This resulted in each component being a 1:3:3:1 quartet with  $^4J(^1\text{H}-^{29}\text{Si}-^{31}\text{P}-^{28}\text{Si}-^1\text{H})$  equal to  $1 \text{ Hz} \pm 0.2 \text{ Hz}$ . The "inner" satellites caused by  $^{29}\text{Si}-^{31}\text{P}-^{28}\text{Si}-\text{H}$  coupling were not observed since they were too close to the main signal to be properly resolved (see  $^1\text{H}-(^{29}\text{Si})$  INDOR).

As before an  $^1\text{H}-(^{29}\text{Si})$  INDOR spectrum was recorded. It showed a basic 1:3:3:1 quartet with a  $^{29}\text{Si}-\text{H}$  coupling of  $188 \pm 4$  Hz. Each member of the quartet was also split into a 1:3:3:1 quartet with a coupling of  $7.5 \pm 0.5$  Hz. This additional coupling was  $^3J(^{29}\text{Si}-^{31}\text{P}-^{28}\text{Si}-^1\text{H})$ . (see figure 3.16). Relative signs of some coupling constants could also be obtained and a value of  $^1J(^{31}\text{P}-^{29}\text{Si})$  could also be determined as follows:-

Each member of the  $^{29}\text{Si}$  satellite doublet was used to generate an  $^1\text{H}-(^{29}\text{Si})$  INDOR spectrum. The two spectra obtained were identical except that corresponding lines in each were at different frequencies. This difference was  $^1J(^{31}\text{P}-^{29}\text{Si})$  which had a value of  $256 \pm 2$  Hz. It was also found that using the  $^{29}\text{Si}$  satellite, observed to low frequency, to generate the  $^1\text{H}-(^{29}\text{Si})$  INDOR spectrum gave the high frequency  $^{29}\text{Si}$  values. This means that  $^1K(^{31}\text{P}-^{29}\text{Si})$  has the opposite sign to  $^2K(^{31}\text{P}-^{29}\text{Si}-\text{H})$  and so  $^1J(^{31}\text{P}-^{29}\text{Si})$  must have the same sign

FIGURE 3.15

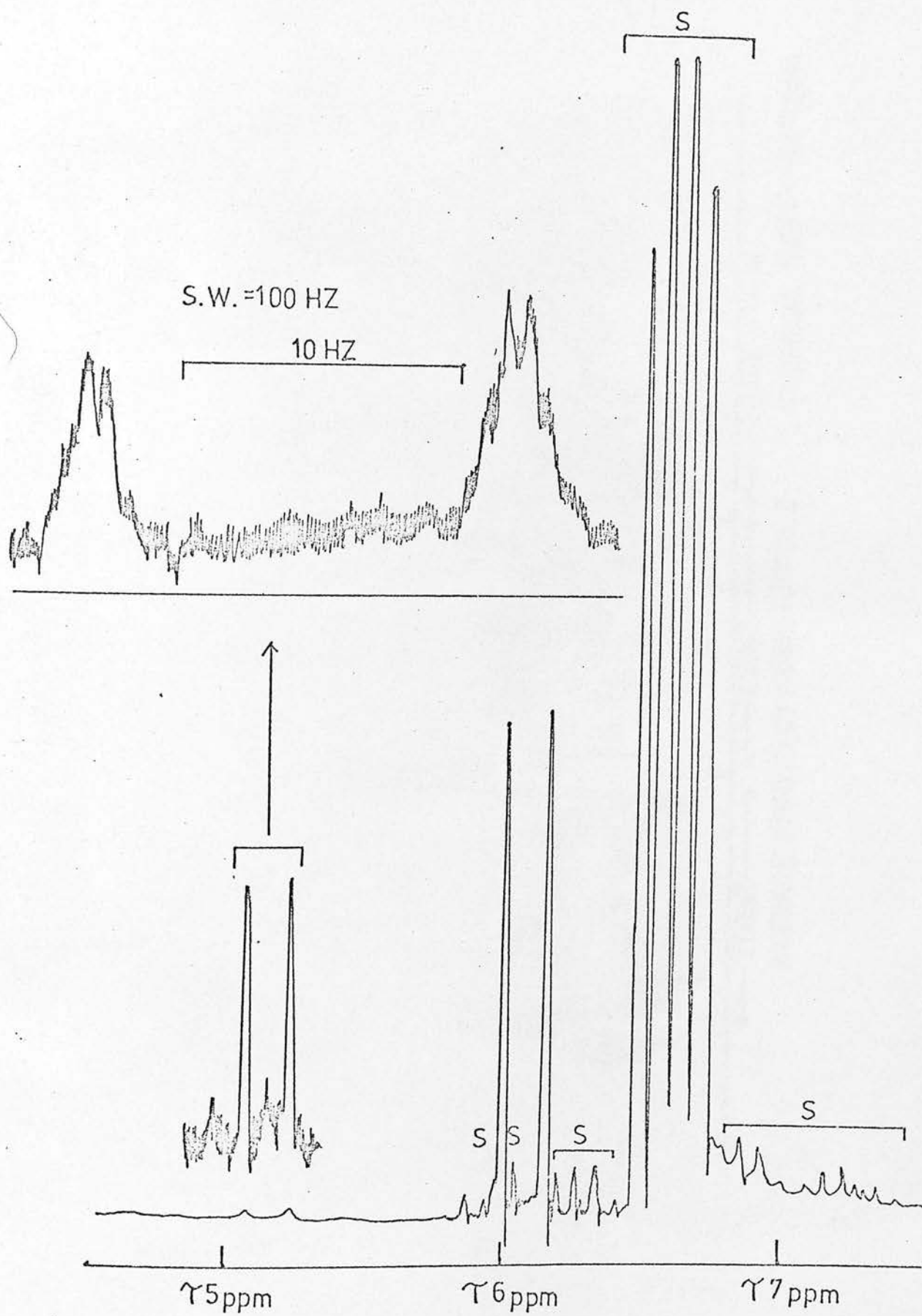


FIGURE 3.16

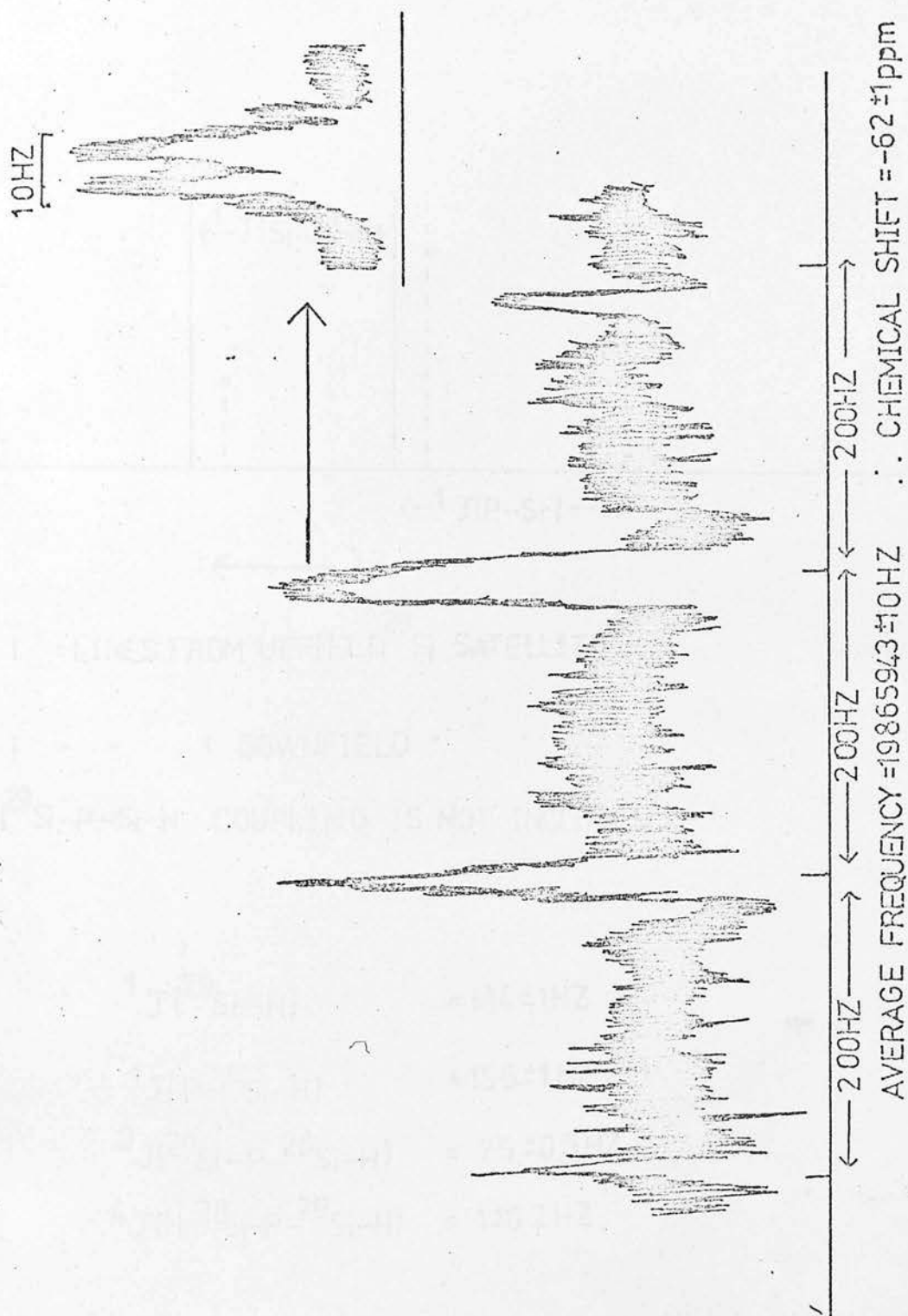
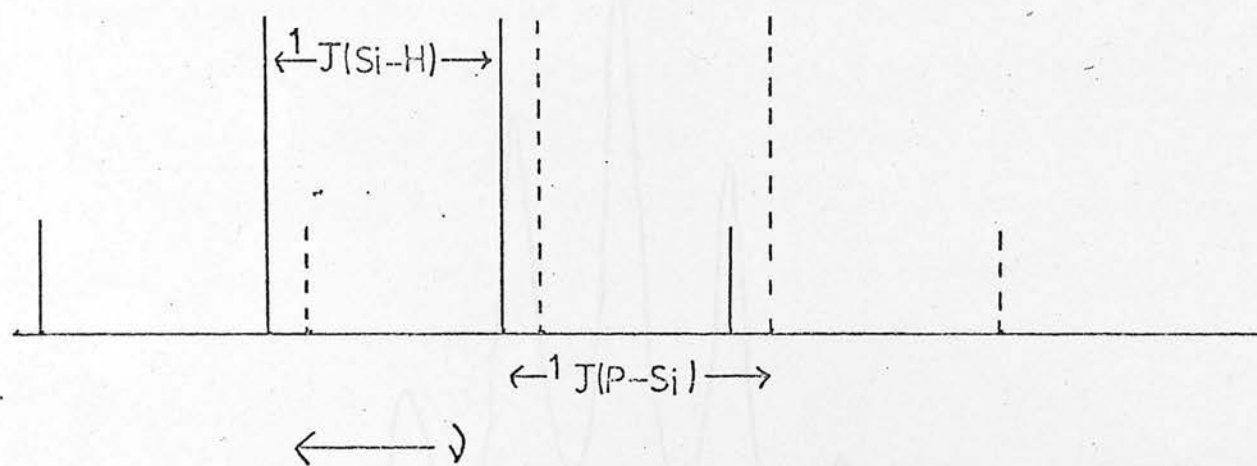


FIGURE 3.16(a)



| = LINES FROM UPFIELD  $^{29}\text{Si}$  SATELLITE

: = " " DOWNFIELD " "

( $^{29}\text{Si-P-Si-H}$  COUPLING IS NOT INCLUDED.)

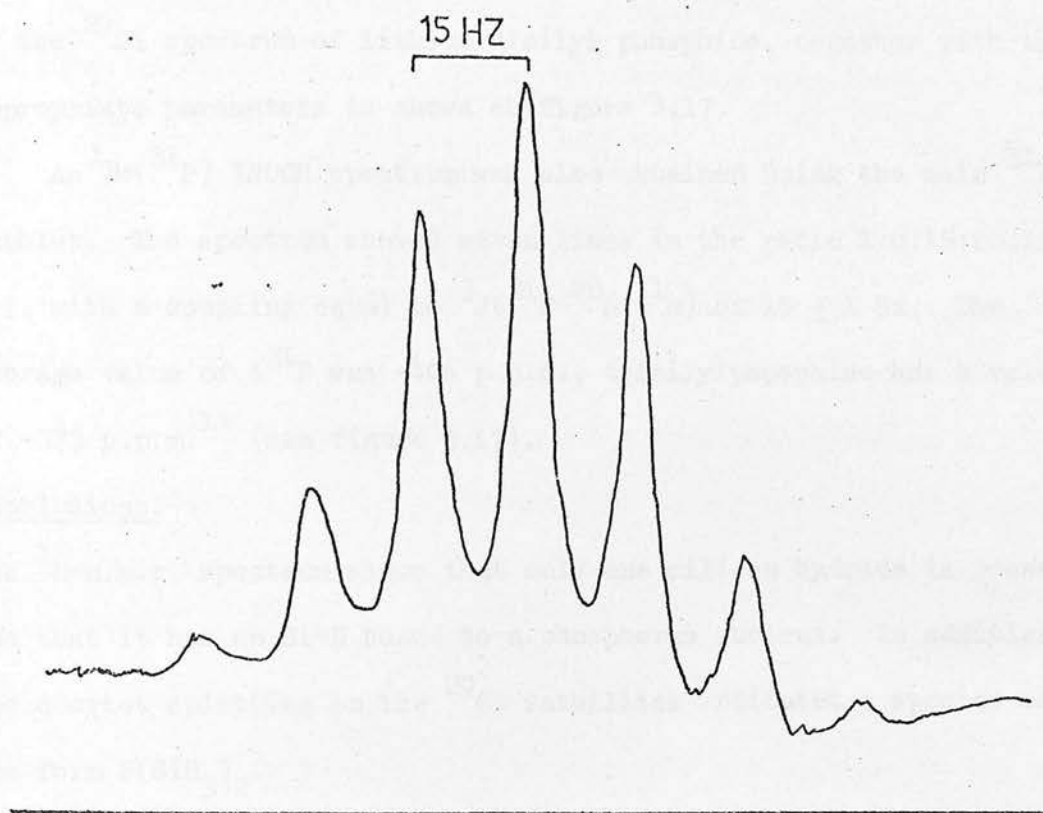
$$^1J(^{29}\text{Si-H}) = 184 \pm 1 \text{ Hz}$$

$$^1J(\text{P-}^{29}\text{Si-H}) = 155 \pm 1 \text{ Hz}$$

$$^3J(^{29}\text{Si-P-}^{28}\text{Si-H}) = 7.5 \pm 0.5 \text{ Hz}$$

$$^4J(\text{H-}^{28}\text{Si-P-}^{29}\text{Si-H}) = 1 \pm 0.2 \text{ Hz}$$

FIGURE 3.17



MEAN FREQUENCY  $= 40464323 \pm 10$  HZ

$\therefore$  CHEMICAL SHIFT  $= -405.7 \pm 0.5$  ppm



$^2J(^{31}\text{P}-^{29}\text{Si}-^1\text{H})$ . Since  $^2K(^{31}\text{P}-^{29}\text{Si}-^1\text{H})$  is normally positive<sup>12</sup> then  $^1K(^{31}\text{P}-^{29}\text{Si})$  must be negative and so  $^1J(^{31}\text{P}-^{29}\text{Si})$  must be positive.

It is interesting to note that direct observation of the  $^{29}\text{Si}$  resonance would not have given as much information so easily. A representation of the  $^{29}\text{Si}$  spectrum of lithium disilyl phosphide, together with the appropriate parameters is shown on figure 3.17.

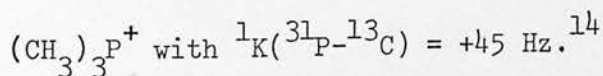
An  $^1\text{H}-(^{31}\text{P})$  INDOR spectrum was also obtained using the main  $^{31}\text{P}$  doublet. The spectrum showed seven lines in the ratio 1:6:15:20:15:6:1, with a coupling equal to  $^3J(^{31}\text{P}-^{28}\text{Si}-^1\text{H})$  of  $15 \pm 1$  Hz. The average value of  $\delta^{31}\text{P}$  was -406 p.p.m., trisilylphosphine has a value of -373 p.p.m.<sup>13</sup> (see figure 3.17).

### Conclusions.

The  $^1\text{H}$ -n.m.r. spectrum shows that only one silicon hydride is present and that it has an Si-H bound to a phosphorus nucleus. In addition, the quartet splitting on the  $^{29}\text{Si}$  satellites indicates a species of the form  $\text{P}(\text{SiH}_3)_2$ .

The  $^1\text{H}-(^{29}\text{Si})$  INDOR spectrum reinforces the conclusion above and the  $^1\text{H}-(^{31}\text{P})$  INDOR spectrum showing six equivalent protons splitting the  $^{31}\text{P}$  resonance, makes it almost conclusive that the white solid can be formulated as lithium disilyl phosphide.

A tentative rationalisation of the sign of  $^1K(^{31}\text{P}-^{29}\text{Si})$  can be made. It has been postulated that a positive value of  $^1K(^{31}\text{P}-\text{X})$ , where X is any nucleus, indicates a lot of positive charge on a phosphorus in a low oxidation state e.g.



the reverse case also holds and so the large negative value for  $^1K(^{31}\text{P}-^{29}\text{Si})$  in lithium disilyl phosphide indicates a large amount of negative charge on the phosphorus atom.

(b) Infrared spectroscopy.

A solid phase i.r. of the white material was recorded using the techniques described previously. The spectrum obtained was consistent with the formulation of this compound as lithium disilyl phosphide, using some of the vibrations of trisilylphosphine for comparison (see figure 3.18 and table 3.8)<sup>15</sup>

(c) Raman spectroscopy.

A Raman spectrum of the white material was obtained as before. The spectrum and data obtained are shown in figure 3.19 and table 3.9. Again using trisilylphosphine as a guide this spectrum was consistent with the formulation of the white material as lithium disilyl phosphide.

A Raman spectrum of the solid material as a solution in diethyl ether. The spectrum and data obtained are shown in figure 3.20 and table 3.10. It should be noted that the bands at 470 and 495  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{sym}} \text{PSi}_2$  and  $\nu_{\text{asy}} \text{PSi}_2$  respectively and that the former is polarised while the latter is not, as one would expect for a molecule belonging to the point group  $\text{C}_{2v}$ .

Conclusions

Vibrational spectra of the white material are consistent with its formulation as lithium disilyl phosphide.

Overall conclusions

The reaction of methyl lithium and excess trisilylphosphine produces lithium disilyl phosphide in high yield.

Experiment 3.5

The Preparation and characterisation of  
lithium disilyl arsenide.

FIGURE 3.18

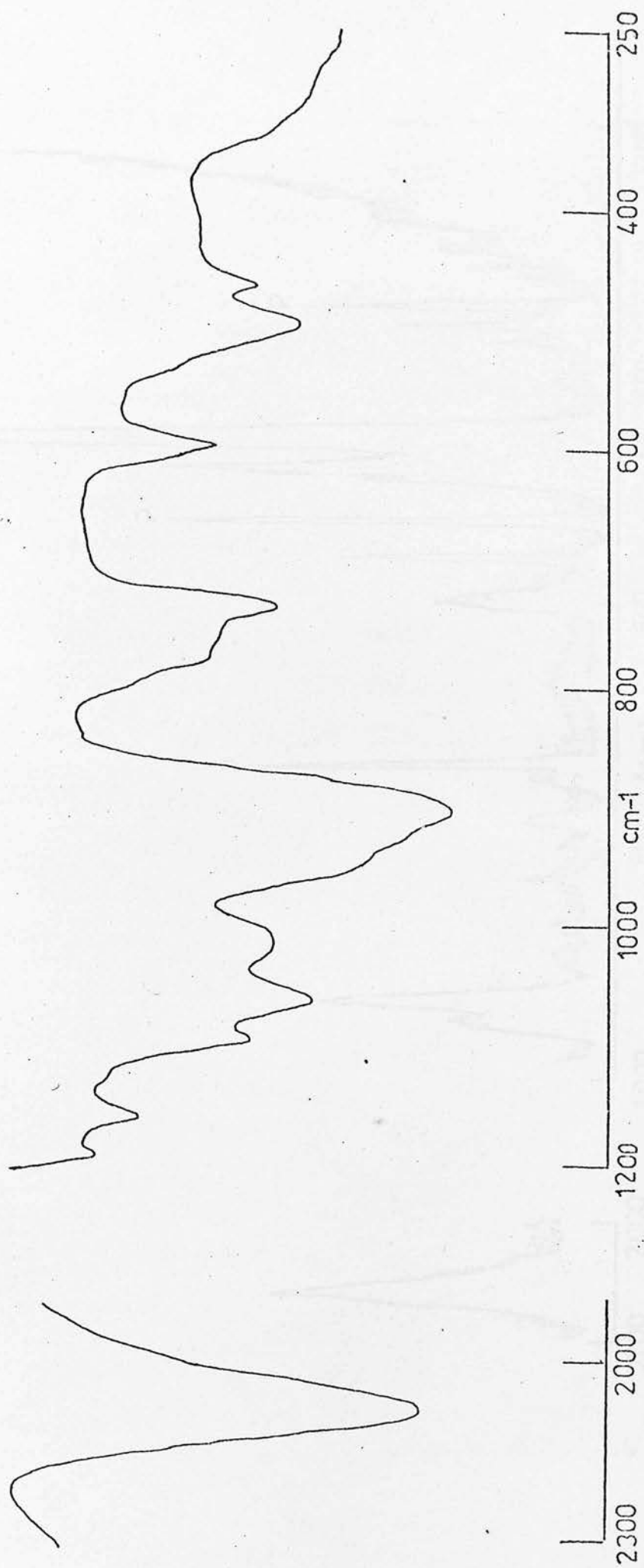


FIGURE 3.19

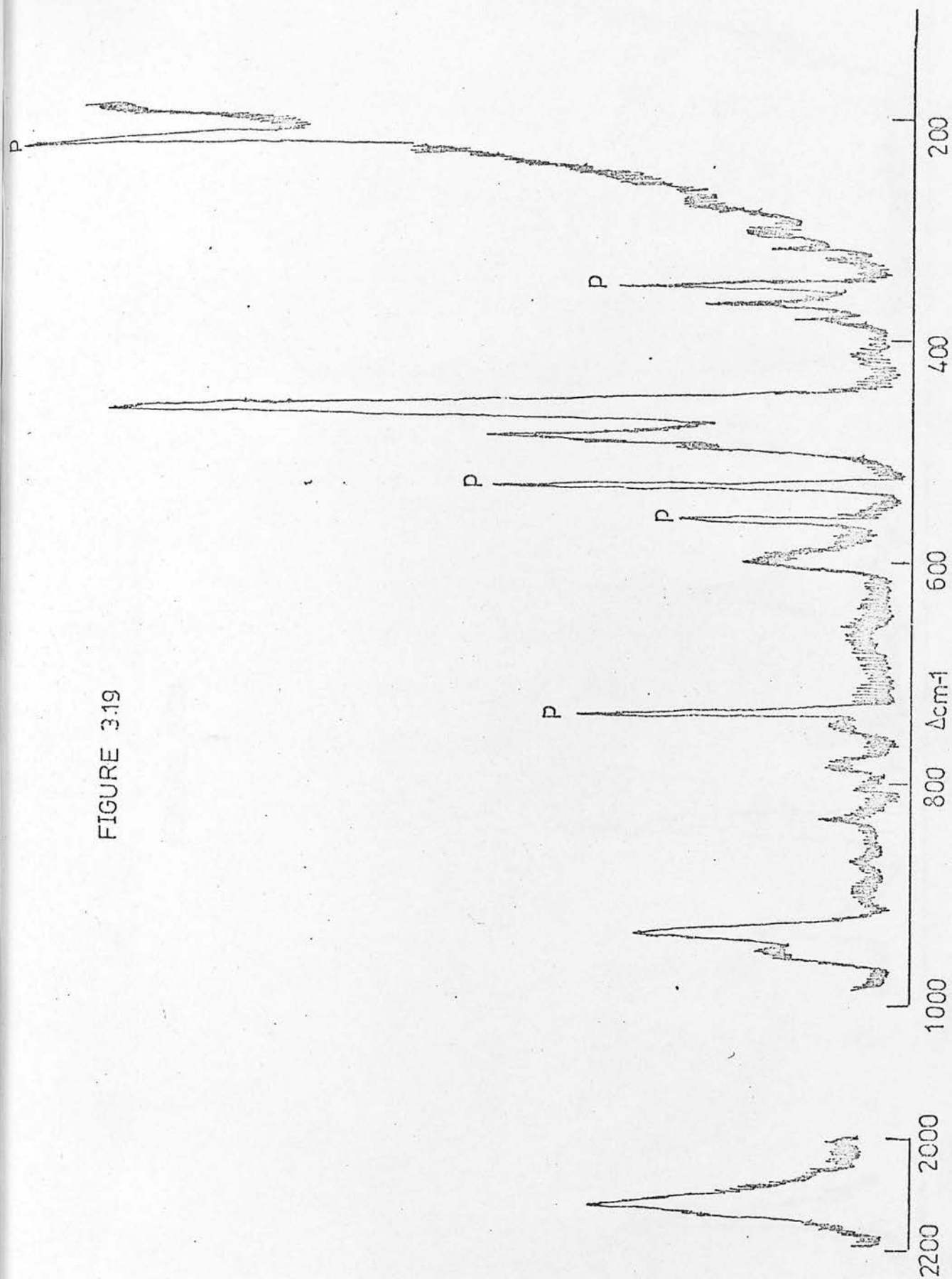


FIGURE 3.20

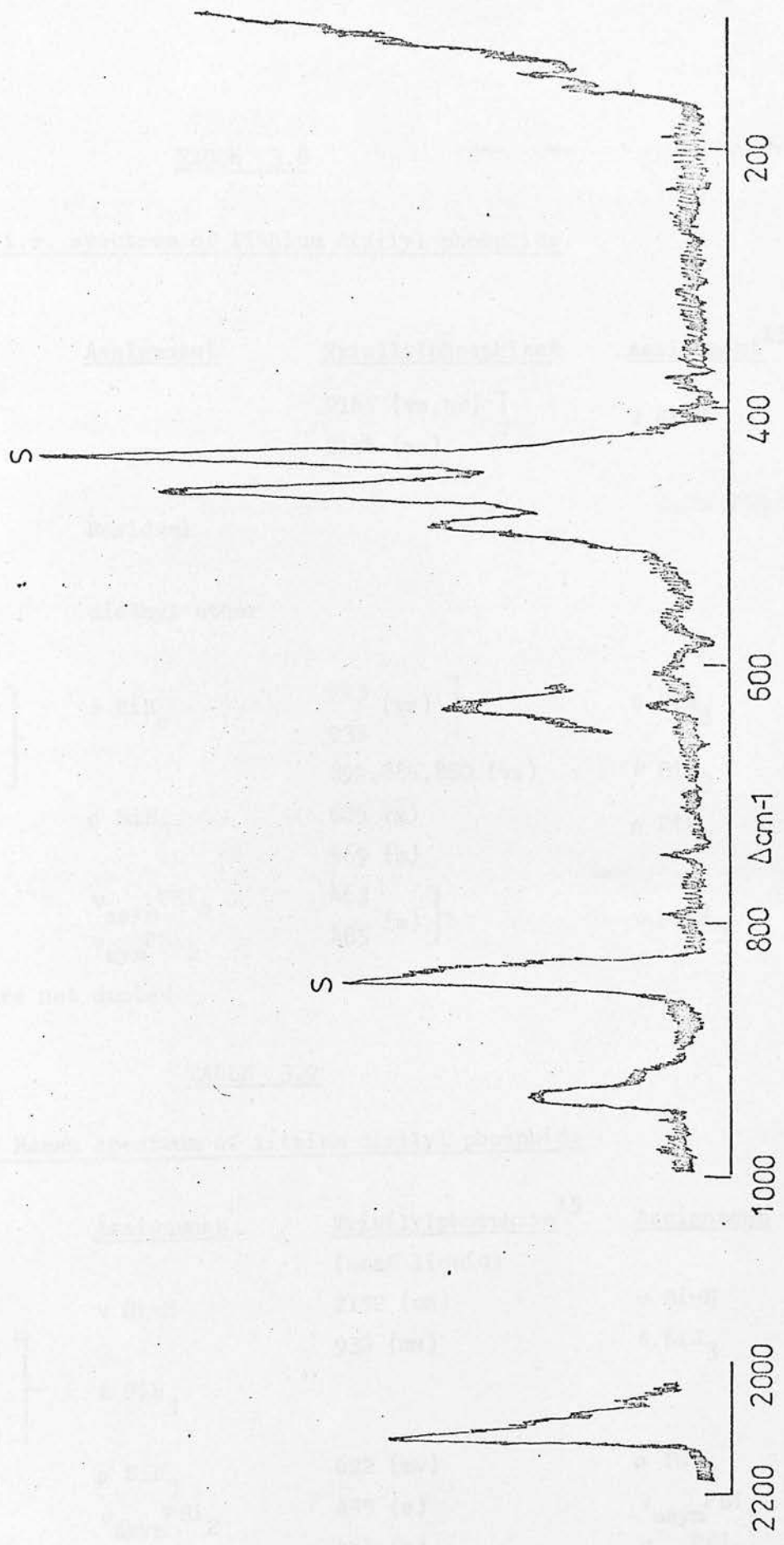


TABLE 3.8

The i.r. spectrum of lithium disilyl phosphide

$\text{cm}^{-1} \pm 5$	Assignment	Trisilylphosphine*	Assignment <sup>15</sup>
2085 (vs)		2165 (vs, br) ] 2154 (vs) ]	$\nu$ Si-H
1185 (vw) ] 1155 (w) ] 1090 (vw) ] 1060 (m) ] 1010 (w) ]	Residual  diethyl ether		
945 (shoulder) ] 925 (shoulder) ] 905 (s) ]	$\delta$ SiH <sub>e</sub>	943 (vs) ] 935 ] 892, 885, 880 (vs)	$\delta$ SiH <sub>3</sub> $\delta$ SiH <sub>3</sub>
600 (m)	$\rho$ SiH <sub>3</sub>	625 (m) 569 (m)	$\rho$ SiH <sub>3</sub>
495 (m) 460 (mw)	$\nu_{\text{asym}}$ PSi <sub>2</sub> $\nu_{\text{sym}}$ PSi <sub>2</sub>	463 ] 465 (m) ]	$\nu$ P-Si <sub>3</sub>

\* weak bands are not quoted.

TABLE 3.9

The Raman spectrum of lithium disilyl phosphide

$\Delta\text{cm}^{-1} \pm 5$	Assignment	Trisilylphosphine <sup>15</sup> (neat liquid)	Assignment
2105(s)	$\nu$ Si-H	2152 (ms)	$\nu$ Si-H
950 (shoulder) ] 935 (m) ] 905 (shoulder) ]	$\delta$ SiH <sub>3</sub>	932 (mw)	$\delta$ SiH <sub>3</sub>
600 (w.br.)	$\rho$ SiH <sub>3</sub>	622 (mw)	$\rho$ SiH <sub>3</sub>
485 (m) 460 (s)	$\nu_{\text{asym}}$ PSi <sub>2</sub> $\nu_{\text{sym}}$ PSi <sub>2</sub>	455 (s) 414 (s) 134 (w.br.)	$\nu_{\text{asym}}$ PSi <sub>3</sub> $\nu_{\text{sym}}$ PSi <sub>3</sub> $\delta_{\text{sym}}$ PSi <sub>3</sub>



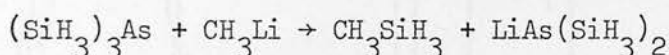
TABLE 3.10

The Raman spectrum of lithium disilyl phosphide as  
a solution in diethyl ether.

$\Delta\text{cm}^{-1} \pm 5$	Assignment	Trisilylphosphine <sup>15</sup> (neat liquid)	Assignment
210 (s.pol)	$\nu$ Si-H	2152 vs	$\nu$ Si-H
955 (shoulder, depol)	$\left[ \begin{array}{l} \delta \text{ SiH}_3 \end{array} \right.$	932 (ms, pol)	$\delta \text{ SiH}_3$
935 (m.br., depol)			
900 (w. shoulder, depol)			
N.O.		622 (mw)	$\rho \text{ SiH}_3$
495 (m. depol)	$\nu_{\text{asym}} \text{PSi}_2$	455 (ms, depol)	$\nu_{\text{asym}} \text{PSi}_3$
470 (m. pol)	$\nu_{\text{sym}} \text{PSi}_2$	414 (s. pol)	$\nu_{\text{sym}} \text{PSi}_3$
		134 (w. br)	$\delta_{\text{sym}} \text{PSi}_3$

In a typical reaction, methyl lithium (0.5m mole) as a molar solution in diethyl ether, was added to an ampoule fitted with a greaseless tap. Trisilylarsine (0.7m mole) was distilled into the ampoule and the reaction allowed to take place at  $-64^{\circ}$  for thirty minutes. The volatile products were removed and isolated by trap to trap distillation. They consisted of silane (0.1m mole) which passed  $-160^{\circ}$ , methyl silane (0.4m mole) which passed  $-120^{\circ}$  but stopped at  $-160^{\circ}$  and the excess trisilylarsine (0.2m mole) which stopped at  $-78^{\circ}$ . Products were identified by their i.r. spectra<sup>1,2,11</sup>. A small amount of hydrogen was detected but no methane.

A very pale yellow solid was produced which dissolved easily in diethyl ether. This solid was considered to be lithium disilyl arsenide mixed with the lithium halide initially present in the methyl lithium. The overall reaction was considered to be:



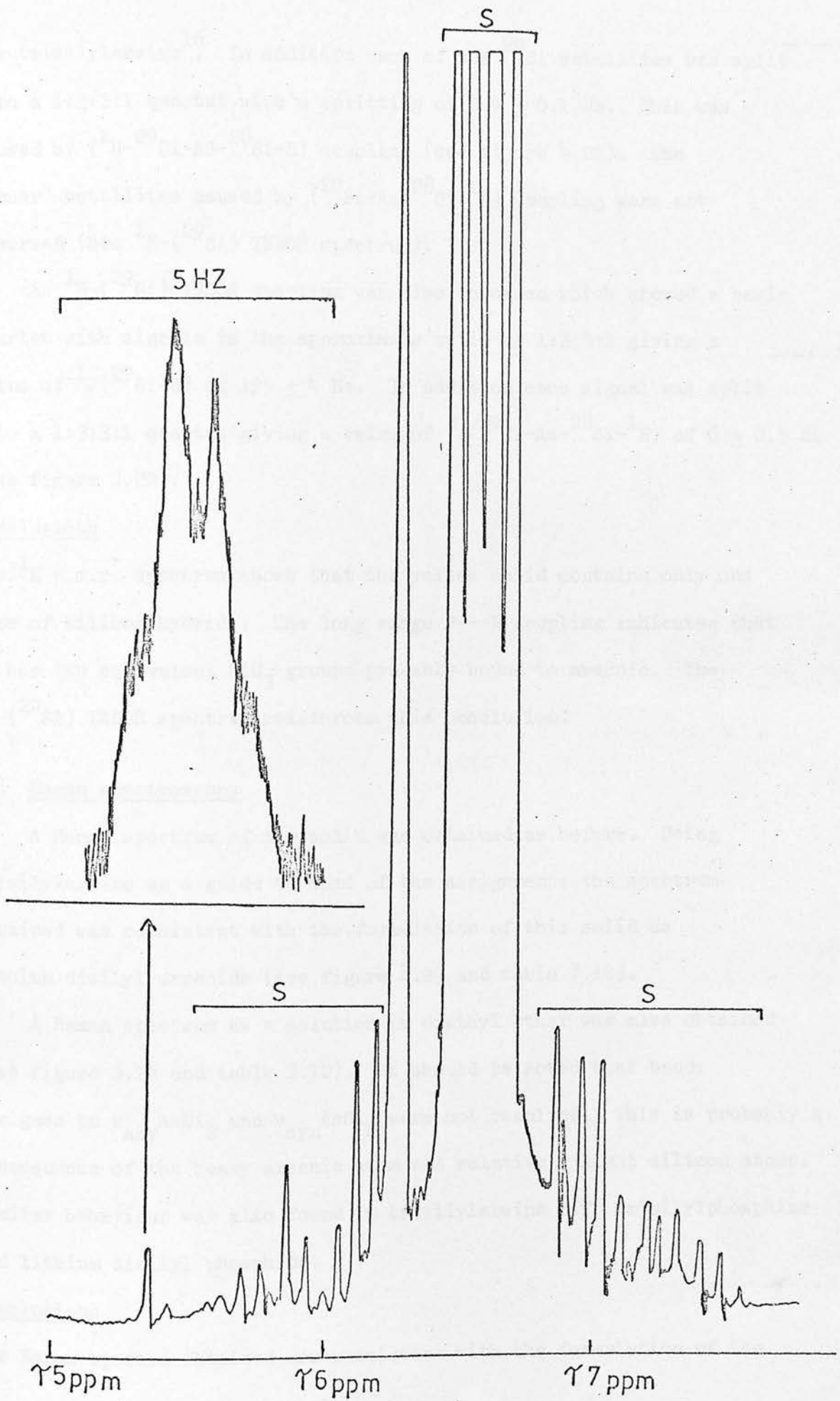
The yield of the silyl anion, based on the amount of methyl lithium and trisilylarsine used and the amount of methyl silane produced was about 80%.

Evidence for the formation of lithium disilyl arsenide by the above reaction was afforded by n.m.r. and Raman spectroscopy. Again, elemental analysis could not be used. Details of the evidence are given below.

(a) Nuclear magnetic resonance.

The yellow solid was prepared by the reaction of methyl lithium and trisilylarsine as before. The  $^1\text{H}$ -n.m.r. spectrum of the solid was recorded using diethyl ether as a solvent. This showed only one silicon hydride to be present with its main signal at  $6.25 \pm 0.02$  p.p.m. and a  $^{29}\text{Si}$  satellite  $97 \pm 0.5$  Hz downfield associated with it. The other satellite was obscured by solvent signals. The value of  $^1J(^{29}\text{Si-H})$  was  $194 \pm 1$  Hz as compared to 6.01 p.p.m. and  $^1J(^{29}\text{Si-H})$  of 210.8 Hz

FIGURE 3.21



for trisilylarsine<sup>16</sup>. In addition each of the  $^{29}\text{Si}$  satellites was split into a 1:3:3:1 quartet with a splitting of  $0.9 \pm 0.1$  Hz. This was caused by ( $^1\text{H}$ - $^{29}\text{Si}$ -As- $^{28}\text{Si}$ -H) coupling (see figure 4.21). The "inner" satellites caused by ( $^{29}\text{Si}$ -As- $^{28}\text{Si}$ - $^1\text{H}$ ) coupling were not observed (see  $^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR spectrum).

An  $^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR spectrum was also recorded which showed a basic quartet with signals in the approximate ratio of 1:3:3:1 giving a value of  $^1J(^{29}\text{Si}$ -H) of  $195 \pm 4$  Hz. In addition each signal was split into a 1:3:3:1 quartet giving a value of  $^3J(^{29}\text{Si}$ -As- $^{28}\text{Si}$ - $^1\text{H}$ ) of  $6 \pm 0.5$  Hz (see figure 3.22).

### Conclusions

The  $^1\text{H}$ -n.m.r. spectrum shows that the yellow solid contains only one type of silicon hydride. The long range H---H coupling indicates that it has two equivalent  $\text{SiH}_3$  groups probably bound to arsenic. The  $^1\text{H}$ -( $^{29}\text{Si}$ ) INDOR spectrum reinforces this conclusion.

### (b) Raman spectroscopy

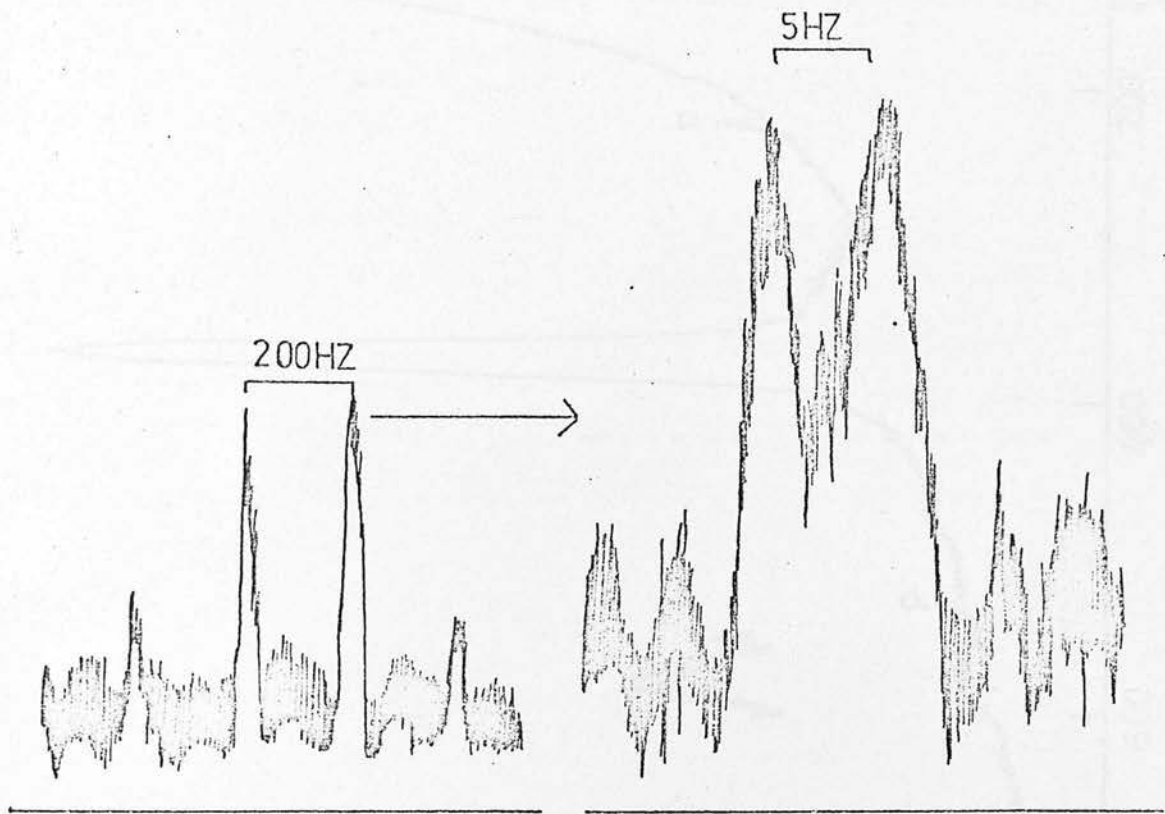
A Raman spectrum of the solid was obtained as before. Using trisilylarsine as a guide to some of the assignments the spectrum obtained was consistent with the formulation of this solid as lithium disilyl arsenide (see figure 3.23 and table 3.10).

A Raman spectrum as a solution in diethyl ether was also obtained (see figure 3.24 and table 3.12). It should be noted that bands assigned to  $\nu_{\text{asy}} \text{AsSi}_2$  and  $\nu_{\text{sym}} \text{AsSi}_2$  were not resolved. This is probably a consequence of the heavy arsenic atom and relatively light silicon atoms. Similar behaviour was also found in trisilylarsine c.f. trisilylphosphine and lithium disilyl phosphide.

### Conclusions

The Raman spectra obtained are consistent with the formulation of the

FIGURE 3.22



MEAN FREQUENCY =  $19865703 \pm 10$  Hz

CHEMICAL SHIFT =  $-75 \pm 1$  ppm

FIGURE 3.23





FIGURE 3.24

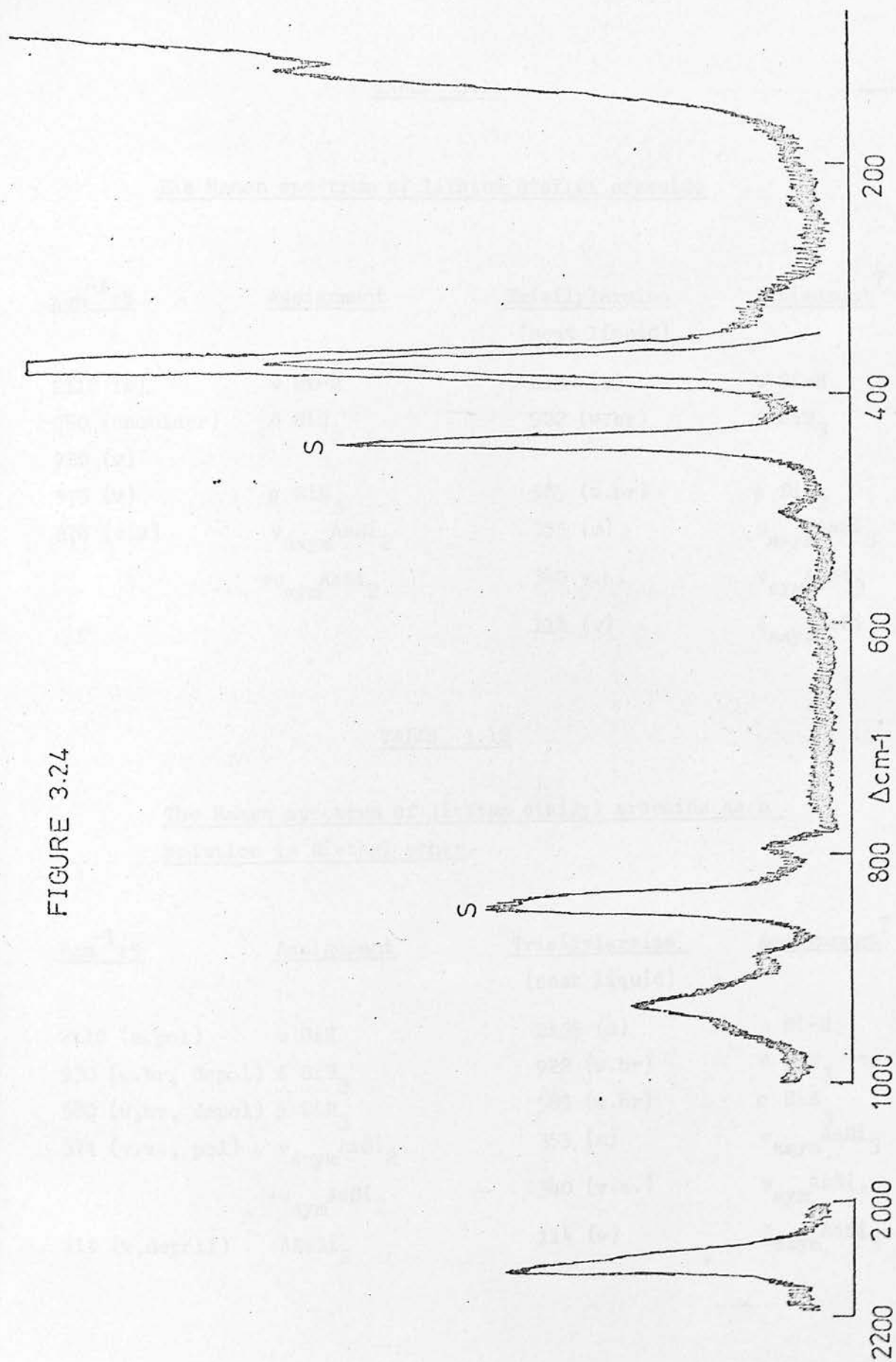


TABLE 3.11

The Raman spectrum of lithium disilyl arsenide

$\Delta\text{cm}^{-1} \pm 5$	Assignment	Trisilylarsine (neat liquid)	Assignment <sup>7</sup>
2110 (m)	$\nu$ Si-H	2135 (s)	$\nu$ Si-H
950 (shoulder)	$\delta$ SiH <sub>3</sub>	922 (w.br)	$\delta$ SiH <sub>3</sub>
930 (w)			
575 (w)	$\rho$ SiH <sub>3</sub>	585 (w.br)	$\rho$ SiH <sub>3</sub>
374 (v.s)	$\nu_{\text{asym}}^{\text{AsSi}_2}$	355 (m)	$\nu_{\text{asym}}^{\text{AsSi}_3}$
	$+\nu_{\text{sym}}^{\text{AsSi}_2}$	340 v.s.	$\nu_{\text{sym}}^{\text{AsSi}_3}$
-		114 (w)	$\delta_{\text{asym}}^{\text{AsSi}_3}$

TABLE 3.12

The Raman spectrum of lithium disilyl arsenide as a solution in diethyl ether.

$\Delta\text{cm}^{-1} \pm 5$	Assignment	Trisilylarsine (neat liquid)	Assignment <sup>7</sup>
2110 (m.pol)	$\nu$ SiH	2135 (s)	$\nu$ Si-H
930 (m.br, depol)	$\delta$ SiH <sub>3</sub>	922 (w.br)	$\delta$ SiH <sub>3</sub>
580 (w,br, depol)	$\rho$ SiH <sub>3</sub>	585 (w.br)	$\rho$ SiH <sub>3</sub>
374 (v.w., pol)	$\nu_{\text{asym}}^{\text{AsSi}_2}$	355 (m)	$\nu_{\text{asym}}^{\text{AsSi}_3}$
	$+\nu_{\text{sym}}^{\text{AsSi}_2}$	340 (v.s.)	$\nu_{\text{sym}}^{\text{AsSi}_3}$
112 (w, depol?)	$\delta\text{AsSi}_2$	114 (w)	$\delta_{\text{asym}}^{\text{AsSi}_3}$

white material as lithium disilyl arsenide.

Overall conclusions

The reaction of methyl lithium and excess trisilylarsine produce lithium disilyl arsenide in high yield.

## PART C

### THE STABILITY OF THE SILYL ANIONS OVER A PERIOD OF TIME.

## INTRODUCTION

It is not unusual for silyl compounds to decompose at room temperature over a period of time. The lithium anions prepared here were found to be quite stable over short periods of time. It is possible that they could decompose over long periods perhaps by a slow reaction with solvent. Using lithium silyl selenide as a typical example this possibility was examined as described below.

### Experiment 3.6

#### The stability of lithium silyl selenide over a period of time.

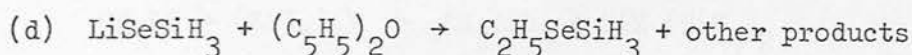
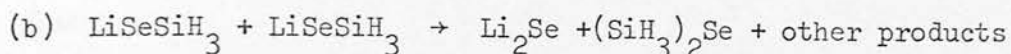
A sample of lithium silyl selenide (0.5m mole) was prepared and an  $^1\text{H}$ -n.m.r. spectrum run as described previously. The spectrum showed only those signals assigned to the silyl anion and the solvent (diethyl ether). The sample was left for ten weeks at room temperature and then the  $^1\text{H}$ -n.m.r. spectrum recorded. It was identical to the one previously obtained. No solid had formed that was insoluble in diethyl ether. The n.m.r. tube was opened using techniques described in Chapter 1, and the volatile products analysed. A trace of silane ( $<0.05\text{m}$  mole), identified by its i.r. spectrum,<sup>1</sup> was detected but no methane. Diethyl ether was the only other compound detected.

The tube was resealed and the solid left at room temperature for a further three months. On opening the tube no non-condensable gas was detected. Fresh diethyl ether was added and all the solid dissolved. Reaction with trimethylsilyl chloride produced trimethylsilyl silyl selenide (0.4m mole) as described previously.

### Conclusions

Lithium silyl selenide is stable as a solid and as a solution in diethyl

ether over long periods. This must mean that the following reactions do not occur

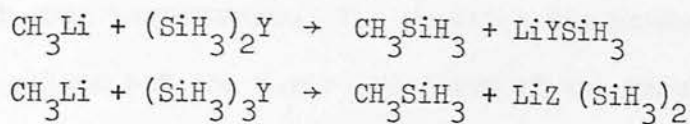


The reason for this stability may well be linked with the structure of the anion as a solid and in solution. The lithium halide present may well be involved as well. It would be interesting to prepare a pure sample of lithium silyl selenide for comparison in view of the fact that pure methyl lithium will react with diethyl ether but the presence of lithium halide markedly reduces the rate of this reaction because of the reduced reactivity of the methyl lithium/lithium halide complex formed.<sup>17</sup>



DISCUSSION OF RESULTS

The preceding experiments have shown that the following reactions take place



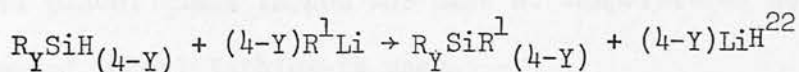
Y = O, S, Se

Z = P, As

This type of cleavage reaction by alkyl lithium reagents is not uncommon. A few examples are shown below.

1.  $(\text{C}_2\text{H}_5)_2\text{O} + \text{CH}_3\text{Li} \rightarrow \text{C}_2\text{H}_5\text{OLi} + \text{C}_2\text{H}_4 + \text{CH}_4^{18}$
2.  $\text{PR}_3 + \text{C}_6\text{H}_5\text{Li} \rightarrow \text{PR}_2\text{Li} + \text{RC}_6\text{H}_5^{19}$
3.  $\text{R}_2\text{PPR}_2 + \text{R}^1\text{Li} \rightarrow \text{LiPR}_2 + \text{R}^1\text{PR}_2^{20}$
4.  $(\text{C}_6\text{H}_5)_3\text{Si}_2 + \text{C}_6\text{H}_5\text{Li} \rightarrow (\text{C}_6\text{H}_5)_4\text{Si} + (\text{C}_6\text{H}_5)_3\text{SiOLi}^{21}$

It is not surprising that lithium silyl anions can be prepared by cleavage by methyllithium. What is surprising is that the yields are very high. It might be expected that methyl lithium would produce methane since the following type of reaction is common.



Y = O→3

R = Alkyl or Aryl.

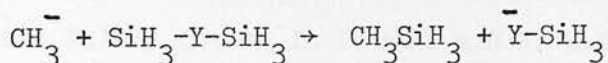
The answer probably lies in the relative reaction rates of the cleavage reaction and the metal-hydrogen exchange. The former is usually much more rapid than the latter. Thus, at  $-64^\circ$  the cleavage reaction is the only one to take place.

It is also interesting that the lithium silyl anions do not either attack diethyl ether or undergo metal-hydrogen exchange with other silyl species present. This must be a question of reactivity possibly

connected with the presence of LITHIUMhalide. However, it has been shown that they will undergo rapid cleavage reactions (see chapter 4).

It is pertinent to note that the reaction of methyl lithium and trisilylamine did not give lithium disilyl amide as an isolable product at room temperature. The reaction did produce the required amount of methyl silane but the n.m.r. spectrum of the resulting white solid showed a broad resonance in the silyl region indicating that a polymer was present. There is some evidence to suggest that lithium disilyl amide is not a stable species at room temperature from reactions between disilyl amine and methyl lithium.<sup>23</sup>

A plausible mechanism for this cleavage reaction involves initial attack by the methyl anion on the silicon (Possibly using "d" orbitals) followed by the Si-Y or Si-Z cleavage to produce methyl silane and the silyl anion.



The resulting anion, would now be kinetically stable to further attack by methyl lithium on simple electro-static grounds. In an excess of  $(\text{SiH}_3)_2\text{Y}$  all the methyl lithium is used up before further attack on the silyl anion takes place. This is not the case at temperatures above  $-64^\circ$  or if excess of methyl lithium is used.

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## CHAPTER 4

PART A            Some reactions of group V and group VI  
silyl anions.

PART B            Some reactions of group V and group VI  
silyl anions with closely related molecules.

PART C            Attempts to modify the reactivity of the  
silyl anions of Group V and Group VI.

## ABSTRACT

The following abstracts are intended to provide a brief summary of the work reported in the following pages. They are not intended to be a substitute for the full text of the report.

The following abstracts are intended to provide a brief summary of the work reported in the following pages. They are not intended to be a substitute for the full text of the report.

## PART A

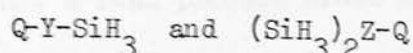
Some reactions of group V and group VI

silyl anions.



## INTRODUCTION

One of the objectives of this work was to provide new synthetic routes to derivatives of the type



where Q is any group of interest. (Y = O, S, Se and Z = P, As).

The following experiments represent attempts to carry out several reactions with a view to assessing the type of problems associated with the use of the silyl anions of group VI and V as synthetic reagents. No detailed analysis of reactions was attempted; the products were merely investigated far enough to decide whether a reaction has given a clear-cut product or not. This approach was considered more useful than studying a relatively small number of reactions in depth in the limited time available.

Some of the reactions were carried out in n.m.r. tubes. This technique has several advantages over working exclusively on a vacuum line some of which are listed below.

- (a) n.m.r. spectroscopy is a non-destructive technique with the added advantage that it does not change the system under study in any way.
- (b) small amounts ( $\sim 0.2$  mole) of starting materials can be used.
- (c) although a product cannot always be positively identified by n.m.r. techniques it can at least be decided if a reaction has many side-reactions or not.
- (d) reaction products can be monitored as the reaction proceeds and over a temperature range from about  $-100^\circ$  to  $+150^\circ$  if required.

The only major disadvantage of this technique was that it was necessary to use diethyl ether as a solvent. This meant that the region from 6.5 to 10 p.p.m. was obscured by the solvent resonances. In practice this was not a real problem since most silicon hydrides have resonances between 5 and 6 p.p.m.

Experiment 4.1The reaction of methyl iodide and lithium silyl sulphide

Lithium silyl sulphide (0.2m moles) was prepared as usual and was allowed to react with methyl iodide (0.3m moles) at room temperature in an n.m.r. tube. Diethyl ether was used as a solvent. A white insoluble product was formed very quickly and the  $^1\text{H}$ -n.m.r. spectrum showed methyl silyl sulphide to be present, even though the methyl resonances were obscured by solvent, since the long range,  $\text{H}\cdots\text{H}$ , coupling was observed.

<u>Observed resonances</u>	<u>Literature<sup>1</sup></u>
$\text{T}(\text{CH}_3)$ - obscured by solvent.	7.92 p.p.m.
$\text{T}(\text{SiH}_3)$ 5.70	5.70 p.p.m.
$^4\text{J}(\text{H-Si-S-C-H}) = 0.45 \pm 0.05 \text{ Hz}$	0.45 Hz

A small amount (10% of total Si-H present, based on relative peak areas) of disilyl sulphide was also present.

Conclusion

Lithium silyl sulphide reacts cleanly with methyl iodide to produce methyl silyl sulphide in high yield (~90%). A small amount of disilyl sulphide and presumably dimethyl sulphide were also produced. The overall reaction was considered to be

Experiment 4.2

The reaction of lithium silyl sulphide and dichloro-  
dimethylsilane.

(a) Lithium silyl sulphide (0.4m moles) was prepared as usual and allowed to react with dichloro-dimethylsilane (0.2m moles) in an n.m.r. tube at  $-78^\circ$ . Diethyl ether was used as solvent. The  $^1\text{H}$ -n.m.r.

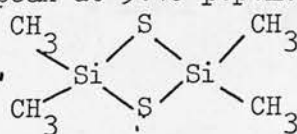
spectrum showed two main signals at 5.67 p.p.m. and 5.75 p.p.m., the relative intensities of which were a function of the reaction time and of temperature. Initially, at  $-78^{\circ}$  the signal at 5.67 p.p.m. was very large while the signal at 5.75 p.p.m. was relatively small. After two hours at  $-35^{\circ}$  the two signals were of comparable intensity and after two hours at  $+28^{\circ}$  the signal at 5.67 p.p.m. was marginally smaller than the other.

It was obvious that using diethyl ether was very restrictive in this particular case. However, it did show that a slow reaction was taking place and at least two products were formed.

The n.m.r. tube was opened using techniques outlined in chapter 1 and the contents fractionated. A mixture of disilyl sulphide and diethyl ether was easily separated from the rest by fractionation at  $-64^{\circ}$ . It was not possible to separate the disilyl sulphide from diethyl ether. The less volatile products consisted of a fairly involatile clear liquid which tended to crystallise easily below room temperature. This sample was condensed into an n.m.r. tube and benzene added as solvent. Previously obscured signals could then be observed. The results are shown below.

<u>Chemical shift (+ 0.01 p.p.m.)</u>	<u>Assignment</u>
5.76 (s)	$(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$
5.86 (trace)	$(\text{SiH}_3)_2\text{S}$
9.46 (m)	$((\text{CH}_3)_2\text{SiS})_2$
9.54 (s)	$(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$

The above assignments are very tentative. The peak at 9.46 p.p.m. is assigned to a tetramethyl cyclodisildithiane,



(compound (A)) on the grounds that a mass spectrum showed this molecule to be present, the exact mass being accurate to within 2 p.p.m.

Observed Mass

179.992062

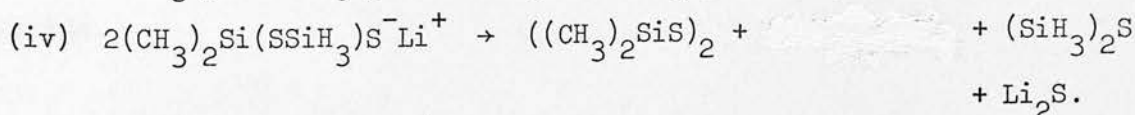
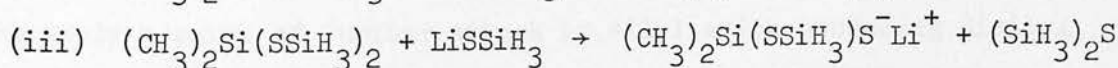
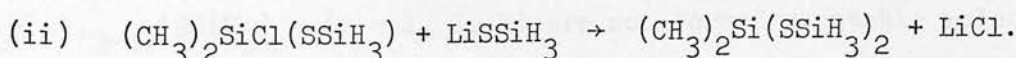
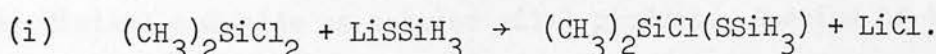
Required Mass for Compound (A)

179.991898

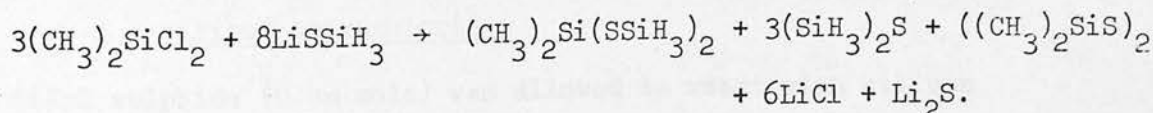
. . . Error. <2 p.p.m.

No mass spectrum for  $(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$  could be obtained because of a contaminated mass spectrometer. However, the resonances at 5.76 and 9.54 p.p.m. are in the ratio of one to one and their chemical shifts suggest a silyl-thio derivative with as many methyl groups as silyl groups. This is consistent with the assignment of these signals to  $(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$ .

(b) The experiment was repeated as before except that the ratio of halide to anion was one to one. The result was a significant increase ( $\sim 50\%$ ) in the proportion of the n.m.r. signal assigned to  $((\text{CH}_3)_2\text{SiS})_2$ . This observation is consistent with the formation of compound (A) as a result of further attack on  $(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$  by excess silyl anion. A possible reaction route is:-



Overall Reaction:-



### Conclusion

Lithium silyl sulphide and chloro-dimethylsilane react to give at least



three products; disilyl sulphide and two others, tentatively assigned as  $(\text{CH}_3)_2\text{Si}(\text{SSiH}_3)_2$  and compound (A). The relative proportions of the three products depends on the initial concentrations of starting materials. Excess of silyl anion favours the formation of compound (A)

#### Experiment 4.3

##### The reaction of lithium silyl sulphide and methyl-trichlorosilane.

Lithium silyl sulphide (0.3m mole) was allowed to react with methyl-trichlorosilane in an n.m.r. tube at  $-78^\circ$  using diethyl ether as a solvent. A fast reaction took place, producing a white solid presumed to be lithium chloride, in which the only major silyl product observed in the  $^1\text{H}$ -n.m.r. spectrum was disilyl sulphide. During the course of the reaction various small resonances in the region 5.7 to 6 p.p.m. were observed: they may represent unstable intermediates.

#### Conclusion

Lithium silyl sulphide and methyl-trichlorosilane react to give only disilyl sulphide as a major silyl product. Species of the type  $\text{CH}_3\text{SiCl}_{(3-n)}(\text{SSiH}_3)_n$ , ( $n = 1, 2, 3$ ) are not formed as stable molecules presumably because of further attack by silyl anion producing disilyl sulphide.

#### Experiment 4.4

##### The reaction of lithium silyl sulphide and silicon tetrachloride.

Lithium silyl sulphide (0.4m mole) was allowed to react with silicon tetrachloride (0.1m mole) in an n.m.r. tube at  $-78^\circ$ . As before a very fast reaction took place producing a white solid presumed to be lithium chloride. The only major silyl compound observed in the resulting



$^1\text{H}$ -n.m.r. spectrum was disilyl sulphide at 5.65 p.p.m. with  $^1J(^{29}\text{Si-H})$  equal to  $225 \pm 1 \text{ Hz}^2$ .

### Conclusion

Lithium silyl sulphide and silicon tetrachloride react to give only disilyl sulphide as a major silyl product. Species of the form  $\text{Cl}_{(4-n)}\text{Si}(\text{SSiH}_3)_n$  ( $n = 1, 2, 3, 4$ ) are not formed as stable molecules presumably because of further attack by silyl anion producing disilyl sulphide.

### Experiment 4.5

#### The reaction of lithium silyl selenide and acetyl chloride.

Lithium silyl selenide (0.4m mole) was prepared in the usual way in an ampoule fitted with a greaseless tap, Diethyl ether ( $\sim 5 \text{ ml}$ ) was used as a solvent. Acetyl chloride (0.5m mole) was condensed into the ampoule and the reaction allowed to proceed for five minutes at  $-64^\circ$ . During the course of the reaction the ampoule was shaken vigorously. The reaction produced a white precipitate, presumed to be lithium halide, and a yellow solution. The volatile products consisted of acetyl silyl selenide\* and disilyl selenide and the solvent diethyl ether. The products were identified by their characteristic i.r. and n.m.r. spectra.<sup>3,4</sup> The solvent was separated by repeated fractionation at  $-64^\circ$ .

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\* This molecule actually exists as an equilibrium mixture of acetyl silyl selenide and seleno-acetyl silyl ether<sup>3</sup> but will be referred to as acetyl silyl selenide and the formula written as  $\text{CH}_3\text{C}(\text{O}, \text{Se})\text{SiH}_3$  for the sake of brevity.

Conclusion

Under the conditions quoted above acetyl silyl selenide can be prepared from lithium silyl selenide and acetyl chloride. The yield of product was about 80% as estimated from the relative areas of n.m.r. signals of acetyl silyl selenide and disilyl selenide. It should be noted that this reaction was very sensitive to the conditions used. Using the reaction conditions given above the proportion of disilyl selenide (and presumably diacetyl selenide) was about 10% (estimated from n.m.r. signals). Any other conditions produced much larger proportions of disilyl selenide. It was also found difficult to scale up this reaction.

The overall reaction was considered to be:

Experiment 4.6

The reaction of lithium silyl sulphide and  
acetyl chloride.

Lithium silyl sulphide (0.4m mole) was prepared as usual in an ampoule fitted with a greaseless tap. The reaction was carried out with acetyl chloride (0.5m mole) as described in the previous experiment. Similar yields of the analogous products were obtained. They were identified by their i.r. and n.m.r. spectra.<sup>3,4</sup>

Conclusion

Acetyl silyl sulphide can be prepared in high yield from the reaction of acetyl chloride and lithium silyl sulphide in diethyl ether at  $-64^\circ$ . The overall reaction was considered to be:

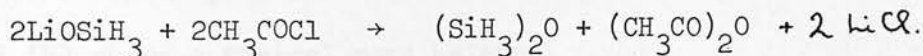


Experiment 4.7The reaction lithium silyl oxide and  
acetyl chloride.

Lithium silyl oxide (0.2m moles) was allowed to react at  $-78^{\circ}$  with acetyl chloride (0.3m moles) in an n.m.r. tube with diethyl ether as solvent. A very fast reaction took place forming a white solid presumed to be lithium chloride. The  $^1\text{H}$ -n.m.r. spectrum (run at  $-78^{\circ}$ ) showed disiloxane as the only silyl product<sup>2</sup> at  $5.39 \pm 0.001$  p.p.m. and  $^1\text{J}(^{29}\text{Si-H})$  equal to  $222 \pm 1$  Hz. No silane or hydrogen was observed.

Conclusion

Lithium silyl oxide and acetyl chloride do not react to give silyl acetate ( $\text{CH}_3\text{CO}_2\text{SiH}_3$ ) as a stable product. The reaction is complicated by the reactivity of lithium silyl oxide or acetyl chloride which causes disiloxane to be produced as the only silyl product. The overall reaction was considered to be:

Experiment 4.8The reaction of lithium silyl selenide and  
acetic anhydride.

Lithium silyl selenide (0.4m moles) was prepared as usual in an ampoule fitted with a greaseless tap. Acetic anhydride (0.4m moles, 0.041 g) was condensed into the ampoule and with diethyl ether as solvent the reaction was allowed to proceed at room temperature. A very rapid reaction took place forming a white precipitate and a yellow solution. The volatile products were identified as acetyl silyl

selenide and silyl acetate by their characteristic i.r. and n.m.r. spectra.<sup>3,5</sup>

Pure samples of each product could be obtained but not quantitatively due to the difficulty of separation. Diethyl ether passed  $-78^{\circ}$  and acetyl silyl selenide could be separated from silyl acetate by fractionation at  $-64^{\circ}$ . The latter passed  $-64^{\circ}$  but stopped at  $-78^{\circ}$ .

The relative yields of the products were found to be a function of the reaction times. Table 4.1 (a) shows the effect of reaction time on the products. It should be stressed that the accuracy of the amounts of the products is in some doubt due to the difficulty of quantitative separation but the trend towards the dominance of silyl acetate as the reaction time increases is still apparent.

Silyl bromide in excess was added to the solid residue of the reaction and using diethyl ether as a solvent a mixture of silyl acetate and acetyl silyl selenide was formed. Again, the relative proportions of these products was a function of the reaction time. Table 4.1 (b) shows a typical mass balance.

### Conclusions

The reaction of acetic anhydride and lithium silyl selenide produces silyl acetate and acetyl silyl selenide. The relative proportions of these products depend on reaction time; silyl acetate is formed in preference to acetyl silyl selenide as the reaction time increases. Addition of excess of silyl bromide to the solid residue of the reaction produces acetyl silyl selenide and silyl acetate.

These reaction products can be rationalised in terms of the following reaction schemes.

TABLE 4.1(a)Reaction Time: 1 minute at room temperature.

Amount of acetic anhydride added	= 1m mole
Amount of lithium silyl selenide added	= 0.9m mole
Amount of acetyl silyl selenide produced	= 0.3m mole
Amount of silyl acetate produced	= 0.4m mole

Reaction Time: 5 minutes at room temperature.

Amount of acetic anhydride added	= 1m mole
Amount of lithium silyl selenide added	= 0.9m mole
Amount of acetyl silyl selenide produced	= 0.1m mole
Amount of silyl acetate produced	= 0.6m mole

TABLE 4.1(b)Reaction Time: 1 minute at room temperature.

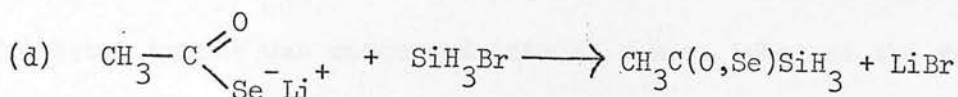
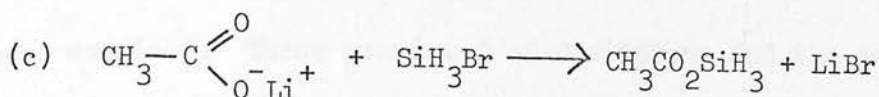
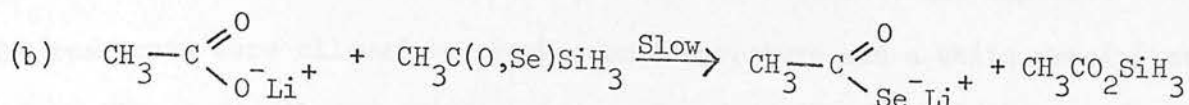
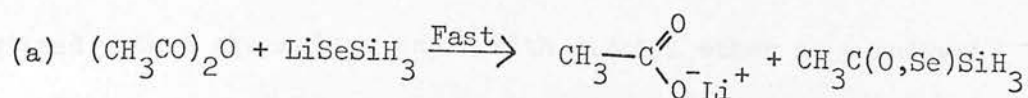
Amount of acetic anhydride added	= 1m mole
Amount of lithium silyl selenide added	= 0.9m mole
Amount of acetyl silyl selenide produced	= 0.3m mole
Amount of silyl acetate produced	= 0.4m mole

After addition of silyl bromide (excess)

Amount of acetyl silyl selenide produced	= 0.4m mole
Amount of silyl acetate produced	= 0.3m mole

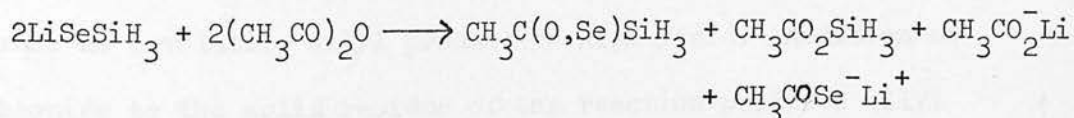
Overall yield of acetyl silyl selenide and silyl acetate = 80%





In a separate experiment lithium acetate (0.4m mole) was prepared in an ampoule fitted with a greaseless tap, and using diethyl ether as a solvent it was allowed to react with acetyl silyl selenide (0.5m mole) at room temperature for five minutes. The volatile products consisted of silyl acetate (0.3 m moles) and the excess of acetyl silyl selenide (0.1m mole). Addition of excess of silyl bromide produced only acetyl silyl selenide (0.3m mole) as product. It was also found that lithium acetate (0.4m mole) reacted with excess of silyl bromide using diethyl ether as solvent to produce silyl acetate (0.3m moles). Thus reactions (b), (c) and (d) can be justified.

The overall reaction was considered to be:



(The relative proportions of products was a function of reaction time.)

#### Experiment 4.9

##### The reaction of lithium silyl oxide and acetic anhydride.

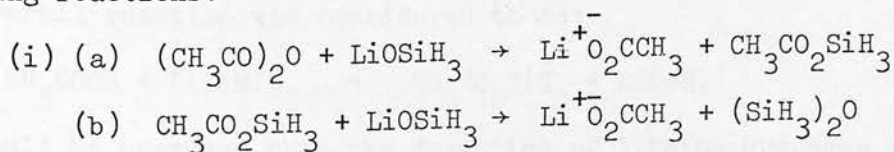
Lithium silyl oxide (0.5m moles) was prepared as usual in an ampoule



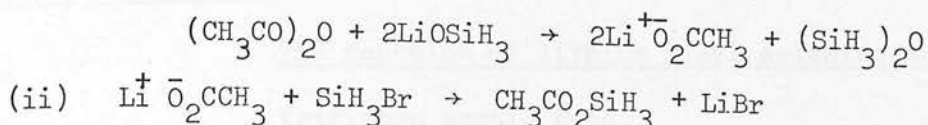
fitted with a greaseless tap. With diethyl ether as a solvent, acetic anhydride (0.5m moles, 0.051 g) was distilled into the ampoule. The reactants were allowed to reach room temperature and a white precipitate formed almost immediately. After a few minutes the volatile products were examined. These consisted of disiloxane and the solvent. Both were identified by their i.r. spectra but could not be separated. The total sample was condensed into an n.m.r. tube and the resulting  $^1\text{H}$ -n.m.r. spectrum showed only disiloxane to be present as a product of this reaction.<sup>2</sup> Using the technique discussed elsewhere, the amount of disiloxane was estimated at about 0.2m moles. The solid residue of the reaction was pumped on for several hours to remove any traces of acetic anhydride left and with fresh solvent excess silyl bromide (1m mole) was added. The reaction was allowed to take place at room temperature for a few minutes and the resulting products fractionated. These consisted of the excess silyl bromide and diethyl ether which passed  $-78^\circ$  while the other product, silyl acetate (0.4m mole), stopped at  $-78^\circ$ . These products were identified by the i.r. spectra.<sup>6,7,5</sup>

### Conclusions

The reaction of lithium silyl oxide and acetic anhydride produces only disiloxane as a volatile silyl product in high yield. Addition of silyl bromide to the solid residue of the reaction produces silyl acetate in high yield. These observations are consistent with the following reactions:-



Overall reaction:-



Reaction (ii) has already been shown to occur (experiment 4.8).

Reaction (i) (a) seems reasonable in the light of experiment 4.8 and reaction (i) (b) reasonable in the light of experiment 4.32. It should be noted that the analogous reaction with lithium silyl selenide does not appear to be important.

#### Experiment 4.10

##### The reaction of lithium silyl selenide and acetic acid.

Acetic acid (0.4m mole) was added to lithium silyl selenide (0.4m mole) in the usual way. Using diethyl ether as a solvent the reaction was allowed to proceed at room temperature for five minutes. A very rapid reaction took place forming a white insoluble solid. The volatile product consisted of silyl acetate, (0.3m mole) identified by its characteristic i.r. spectrum<sup>5</sup> and the solvent ether. No acetyl silyl selenide, disilyl selenide or silane was observed, nor was silyl selenol detected.

#### Conclusion

Silyl acetate can be prepared in high yield (~80%) from lithium silyl selenide and acetic acid. No side reactions appear to take place.

The overall reaction was considered to be:



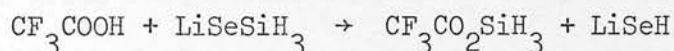
It should be stressed that the formation of lithium hydrogen selenide in this reaction was not demonstrated.

Experiment 4.11The reaction of lithium silyl selenide and trifluoro acetic acid.

This reaction was completely analogous to the preceding one. Lithium silyl selenide (0.4m mole) and trifluoroacetic acid (0.4m moles) produced silyl trifluoroacetate (0.3m mole) identified by its i.r. spectrum<sup>5</sup>.

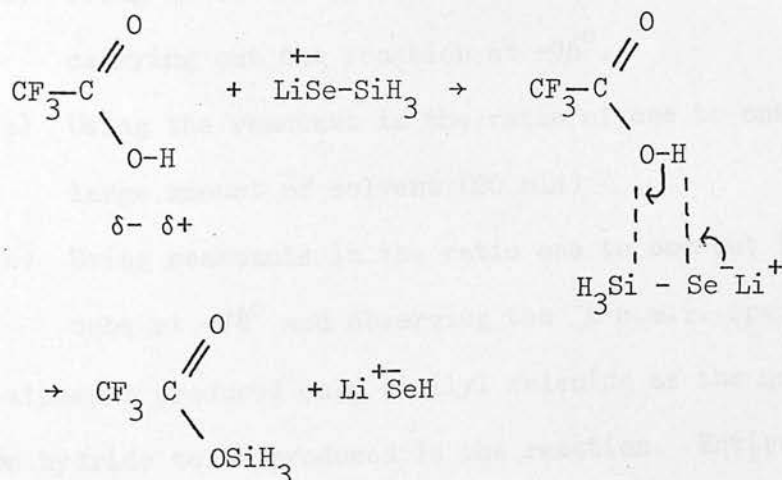
Conclusion

Trifluoro silyl acetate can be prepared in high yield (80%) from the reaction of lithium silyl selenide and trifluoro acetic acid. The overall reaction was considered to be:



Again, the formation of lithium hydrogen selenide was not demonstrated.

A plausible reaction mechanism is:



It is surprising that this reaction goes in such high yield and that no silyl selenol or disilyl selenide is formed. A similar mechanism may well be operating in the preceding reaction

Experiment 4.12The reaction of lithium silyl selenide and  
trifluoroacetyl bromide

Lithium silyl selenide (0.4m mole) was prepared as usual in an ampoule fitted with a greaseless tap. Trifluoroacetyl bromide (0.5m moles) was distilled into the ampoule and using diethyl ether (5 ml) as solvent the reaction was allowed to proceed at  $-96^{\circ}$  for a few minutes. A white precipitate and a bright red solution formed very quickly. The volatile products identified by their i.r. spectra<sup>4,7</sup> consisted of disilyl selenide (0.2m moles) and the solvent. The latter was removed by fractionation at  $-78^{\circ}$ . No  $\text{CF}_3$  derivatives, which usually give distinct group frequencies in their i.r. spectra, could be observed as volatile products.

This reaction was also carried out under a variety of conditions.

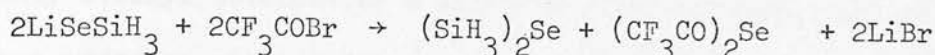
- (a) Using an excess (50%) of trifluoroacetyl bromide and carrying out the reaction at  $-96^{\circ}$ .
- (b) Using the reactant in the ratio of one to one but with a large amount of solvent (20 mls)
- (c) Using reactants in the ratio one to one but in an n.m.r. tube at  $-78^{\circ}$  and observing the  $^1\text{H}$ -n.m.r. spectrum. All

these attempts produced only disilyl selenide as the only observable silicon hydride to be produced in the reaction. Entirely analogous results were found with lithium silyl sulphide.

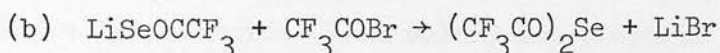
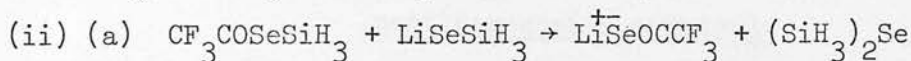
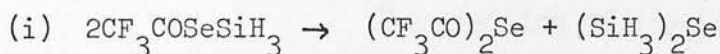
Conclusion

The reaction of trifluoroacetyl bromide and lithium silyl selenide under a variety of conditions produces only disilyl selenide as a reaction product. All the silyl groups added as silyl anion can be accounted for as disilyl selenide in the products. The overall

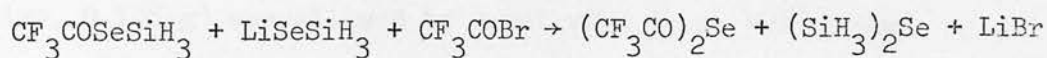
reaction was considered to be:



It should be noted that perfluorodiacetyl selenide was not identified as a reaction produced. However its presence seems likely as a disproportionation product of trifluoroacetyl silyl selenide or as a product of the reaction of lithium trifluoro selenoacetate formed by the reaction of lithium silyl selenide and the derived product and trifluoroacetyl bromide. Both of these reactions were considered to be the main decomposition routes of the desired product.



#### Overall reaction



#### Experiment 4.13

##### The reaction of lithium silyl selenide and Monochloroacetyl chloride

Lithium silyl selenide (0.4m mole) was prepared in the usual way in an ampoule fitted with a greaseless tap. Monochloroacetyl chloride (0.4m moles) was distilled into the ampoule and the reaction allowed to take place at  $-96^\circ$  using diethyl ether as solvent. Disilyl selenide (0.2m moles) identified by its i.r. spectrum<sup>4</sup> was the only volatile silyl product detected. Excess of monochloroacetyl chloride (0.6m moles) gave a similar result. Monobromoacetyl bromide gave completely analogous results.

#### Conclusion

The reaction of lithium silyl selenide and monochloroacetyl chloride



produces only disilyl selenide as a volatile silyl product. All the silyl groups added as silyl anion can be accounted for as disilyl selenide in the products. It seems likely to assume that the desired product, monochloroacetyl silyl selenide, was formed in the early stages of the reaction but that it decomposed along lines similar to those of the preceding reaction. Monobromoacetyl bromide reacts in an analogous way.

#### Experiment 4.14

##### The reaction of lithium silyl selenide and perfluoroacetic anhydride

Lithium silyl selenide (0.4m moles) was prepared in the usual way in an ampoule fitted with a greaseless tap. Perfluoroacetic anhydride (0.5m moles, 0.105 g) was allowed to react with it at  $-78^{\circ}$  using diethyl ether as solvent. A rapid reaction ensued which produced no precipitate and a red solution. On removing the volatile products and the solvent a yellow solid remained. The volatile products consisted of a red material and a small amount of colourless material. At least three volatile compounds could be observed (deduced from i.r. spectra). One of these was identified as silyl trifluoroacetate.<sup>5</sup> Very low yields of products was observed (approximately 10%).

#### Conclusion

The reaction of perfluoroacetic anhydride and lithium silyl selenide does not follow a similar path to the reaction of acetic anhydride and lithium silyl selenide. It is not a clean reaction and may be very complex. The observed effects may well be related to the enhanced reactivity of the carbonyl in the anhydride and the subsequent reaction products



caused by the inductive effect of a  $\text{CF}_3$  group.

#### Experiment 4.15

##### The reaction of lithium disilyl phosphide and acetyl chloride.

(a) Lithium disilyl phosphide (0.2m mole) was prepared according to the method described in chapter 3. Acetyl chloride (0.2m mole) was allowed to react with it in an n.m.r. tube at  $-80^\circ$  using diethyl ether as a solvent. A fast reaction took place giving a yellow solid. The  $^1\text{H}$ -n.m.r. spectrum recorded at  $-80^\circ$  showed a broad resonance centred on 6.05 p.p.m. On Warming the tube to  $-60^\circ$  over a period of thirty minutes no change occurred. However, on warming to  $-30^\circ$  the broad peak changed to two peaks of equal intensity at 5.93 and  $6.18 \pm 0.01$  p.p.m. characteristic of trisilylphosphine. No change occurred in this doublet on cooling to  $-80^\circ$ , the broad peak did not reappear. No silane or hydrogen was observed.

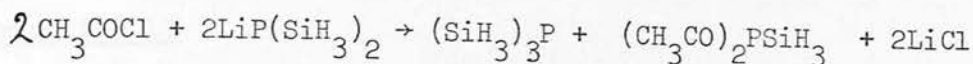
(b) The above reaction was repeated except that an excess (100%) of acetyl chloride was used. The result was exactly the same.

In both experiments the n.m.r. tubes were opened and the volatile products shown to consist of only trisilylphosphine and the solvent ether by their i.r. spectra<sup>8,7</sup>.

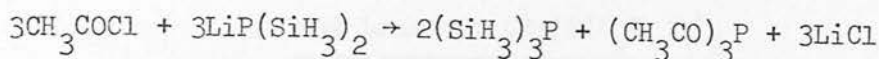
#### Conclusion

The reaction of lithium disilyl phosphide and acetyl chloride does not produce the desired product, acetyl disilylphosphine. Trisilylphosphine seems to be the only volatile silyl product. The observed  $^1\text{H}$ -n.m.r. spectra are consistent with a mixture of lithium silyl anion and trisilylphosphine which slowly changes at higher temperatures to trisilylphosphine. (see experiment 4.34). The overall reaction was

considered to be:



or,



It should be noted that the formation of diacetyl silylphosphine or triacetylphosphine was not demonstrated.

#### Experiment 4.16

##### The reaction of lithium disilyl phosphide and acetic anhydride.

Lithium disilyl phosphide (0.4m mole) was prepared as usual in an ampoule fitted with a greaseless tap. Acetic anhydride (0.4m mole, 0.041 g) was added and the reaction allowed to proceed at  $-24^\circ$  for five minutes using diethyl ether as solvent. A fast reaction took place forming a yellow solid. The volatile products, indentified by their i.r. spectra consisted of trisilylphosphine (0.2m mole) and the solvent ether<sup>8,7</sup>. No evidence for any volatile acetyl compounds could be found. Addition of silyl bromide (1m mole) to the yellow solid using diethyl ether as solvent produced more trisilyl phosphine (0.1m moles).

#### Conclusions

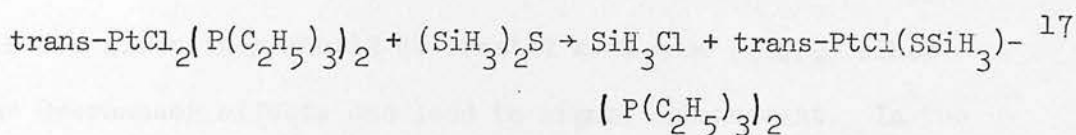
The reaction of acetic anhydride and lithium disilyl phosphide does not produce the desired product, acetyl disilylphosphine. It is likely as with the preceding reaction that it is formed initially but that it is attacked by the reactive silyl anion or by other reaction products e.g. lithium acetate. The result is that trisilylphosphine is produced, with an ether-insoluble, reactive silyl phosphorus anion.

Experiment 4.17

The reaction of lithium silyl sulphide  
and trans-Pt Cl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>

Introduction

Many silyl-platinum derivatives have been prepared and characterised by n.m.r. techniques. For instance, it has been suggested that the following reaction takes place



The following reaction represents an attempt to prepare this product using lithium silyl sulphide <sup>31</sup>P-n.m.r. spectroscopy was used to analyse products since the large <sup>31</sup>P chemical shift range and the characteristic value of <sup>1</sup>J(Pt-P) allows easy and reliable analysis.

Experimental

Lithium silyl **SULPHIDE** (0.3m moles) was prepared as usual and allowed to react with trans-PtCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> (0.4m moles, 0.178g) in an n.m.r. tube at room temperature. Diethyl ether was used as a solvent. A rapid reaction took place with vigorous evolution of a gas. On opening the tube later, this gas was non condensible at liquid nitrogen temperature and so was considered to be hydrogen. Details of the resulting <sup>31</sup>P spectrum obtained are shown below

<u>δ <sup>31</sup>P + 0.1 p.p.m.</u>	<u><sup>1</sup>J(Pt -P)Hz</u>	<u>Relative intensity</u>
5.4	3100	180
5.2	3120	206

Data for other products one might expect from this reaction is given below:

$\delta^{31}\text{P}$	$^1\text{J}(\text{Pt} - \text{P})$	Assignment
22.8	2730	trans-PtHCl(P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>
18.7	2610	trans-PtH(SiH <sub>3</sub> )(P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>
12.3	2457	trans-PtCl <sub>2</sub> (P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>

Several small resonances were observed but none could be assigned to those given above. It should be noted that although relative peak heights are given they should be treated with some caution since nuclear Overhauser effects can lead to signal enhancement. In the case of such similar molecules they are probably a good rough guide to their relative proportions.

#### Conclusion

The reaction of lithium silyl sulphide and trans-PtCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> results in the formation of two main products. These compounds have <sup>31</sup>P chemical shifts of 5.4 and 5.2 p.p.m. In the reaction of disilyl sulphide and trans-PtCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> described in the introduction two peaks at 5.5 and 5.7 p.p.m. were observed in the <sup>31</sup>P n.m.r. spectrum. These have been tentatively assigned to trans-PtClSSiH<sub>3</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> and [trans-PtClSiH<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]<sub>2</sub>S. It seems reasonable to suggest that these are the products observed in this experiment.

#### Experiment 4.18

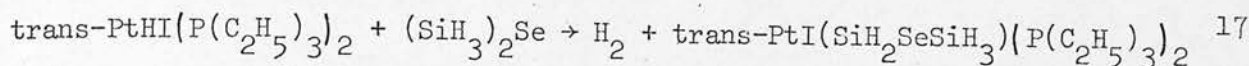
##### The reaction of lithium silyl selenide

##### and trans-PtI<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>

#### Introduction

This reaction was undertaken for similar reasons and in the same way as the previous reaction. Although the desired product, trans-PtI(SiH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> has not been synthesised, similar products

have by the reaction



This particular type of reaction has been much studied.

### Experimental

Lithium silyl selenide (0.4m mole) and trans-PtI<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> (0.5m mole, 0.343g) were allowed to react in an n.m.r. tube as in the previous experiment. Formation of a gas, presumed to be hydrogen was observed. The data obtained from the <sup>31</sup>P n.m.r. spectrum is given below.

<u>Observed</u>				<u>Literature</u> <sup>17</sup>	
$\delta^{31}\text{P} \pm 0.1 \text{ p.p.m.}$	$^1\text{J}(\text{Pt-P})$	<u>Relative Intensity</u>	<u>Assignment</u>	$\delta^{31}\text{P}$	$^1\text{J}(\text{Pt-P})$
20.0	2670	181	H-Pt-I*	19.3	2660
9.9	2460	133	(?)		
9.7	2500	205	[I-Pt-SiH <sub>2</sub> ] <sub>2</sub> Se	9.5	2512
9.5	2520	178	I-Pt-SiH <sub>2</sub> SeSiH <sub>3</sub>	9.1	
0.7	2286	155	I-Pt-I	0.2	2272

\* Triethylphosphine groups are omitted.

Small discrepancies between observed and literature values for  $\delta^{31}\text{P}$  are probably due to solvent shifts.

### Conclusion

This reaction is obviously a complex one and a variety of products are formed, some of which may be the result of reactions of disilyl selenide and not those of the silyl anion. It is always possible to account for the formation of products by elaborate mechanisms but in



this case it is not really justified to do so. The resonance at 9.9 p.p.m. with  $J(\text{Pt-P})$  of 2460 Hz could well be assigned to the desired product  $\text{trans-I-Pt}(\text{SeSiH}_3)(\text{P}(\text{C}_2\text{H}_5)_3)_2$ .

#### Experiment 4.19

##### The reaction of bromo-difluorophosphine and lithium silyl sulphide.

Lithium silyl sulphide (0.2m mole) was prepared as previously described and allowed to react with bromo-difluorophosphine in an n.m.r. tube at  $-78^\circ$ . Diethyl ether was used as a solvent. A very fast reaction took place forming a yellow solution and a white precipitate. The  $^1\text{H}$ -n.m.r. spectrum, recorded at  $-78^\circ$  showed the main reaction products to be disilyl sulphide and silyl fluoride.

<u>Observed Resonance</u>	<u>Assignment</u>	<u>Literature</u>
5.45 p.p.m. $\pm$ 0.01 p.p.m. $^2J(^1\text{H-Si-}^{19}\text{F}) = 46 \pm 1 \text{ Hz}$	] $\text{SiH}_3\text{F}^9$	45.8 $\pm$ 0.02 Hz
5.7 $\pm$ 0.01 p.p.m. $^1J(^{29}\text{Si-H}) = 224 \pm 1 \text{ Hz}$	] $(\text{SiH}_3)_2\text{S}^2$	5.65 p.p.m. 224 p.p.m.

After being warmed to  $-50^\circ$  for fifteen minutes no change was observed. However, on warming to  $-30^\circ$  for a few minutes the peak assigned to disilyl sulphide disappeared and the silyl fluoride resonance increased. No evidence for the formation of the desired product difluorophosphino-silyl sulphide could be detected. The experiment was repeated and the  $^{31}\text{P}$ -n.m.r. spectrum recorded at room temperature. This showed trifluorophosphine (a 1:3:3:1 quartet at  $\delta+106$  with  $^1J(^{31}\text{P-}^{19}\text{F})$  equal to  $1430 \pm 1 \text{ Hz}$ . (Literature



values are  $\delta^{31}\text{P}$  105 p.p.m. and  $^1\text{J}(\text{P-F})$  equal to 1400 Hz<sup>10</sup>) to be present. There ~~were~~ also two peaks at -120 and 150 p.p.m. which could not be assigned. A range of -220 to + 220 p.p.m. was covered.

### Conclusion

Lithium silyl sulphide and bromo-difluorophosphine do not react to give the known compound difluorophosphino silyl sulphide as a stable product; although it may well be formed as an initial product, a further reaction producing disilyl sulphide and insoluble fluorophosphine derivatives takes place. The disilyl sulphide also fluorinated to silyl fluoride. No evidence for the formation of bis(difluorophosphino sulphide) could be detected ( $\delta^{31}\text{P} = -219 \pm 0.1$  p.p.m.<sup>11</sup>).

### Experiment 4.20

#### The reaction of trifluorophosphine and lithium silyl sulphide

Lithium silyl sulphide (0.3m moles) was prepared as usual and allowed to react with trifluorophosphine (0.3m moles) at -78° in an n.m.r. tube. Diethyl ether was used as solvent. A light yellow solution and no precipitate was produced. The  $^1\text{H}$ -n.m.r. spectrum, recorded at -78°, showed a small amount of silyl fluoride and a relatively large amount of disilyl sulphide. On standing for several hours at +28° the silyl fluoride resonance increased at the expense of the resonance assigned to disilyl sulphide. Eventually, silyl fluoride was the only silyl compound that remained. No silane or hydrogen was detected.

### Conclusion

The reaction between lithium silyl sulphide and trifluorophosphine

is initially very fast and produces disilyl sulphide as the main silyl derivative. This is followed by the slow fluorination of disilyl sulphide by an unidentified species, perhaps by an exchange of P-F bonds.

In a separate experiment trifluorophosphine (0.2m moles) and disilyl sulphide (0.2m moles) were sealed in an n.m.r. tube with diethyl ether as solvent. After four days at room temperature no reaction had occurred since the  $^1\text{H}$ -n.m.r. spectrum showed only disilyl sulphide to be present. Thus trifluorophosphine was not the active fluorinating agent in the second part of the above reaction unless a catalyst is present in the system.

#### Experiment 4.21

##### The reaction of mercuric chloride and lithium silyl sulphide.

Lithium silyl sulphide (0.2m moles) was allowed to react with mercuric chloride (0.1m mole, 0.271 g) in an n.m.r. tube at  $-64^\circ$ . Diethyl ether was used as solvent. (see chapter 1 for experimental details). A black precipitate (assumed to be mercuric sulphide) was formed rapidly. The  $^1\text{H}$ -n.m.r. spectrum, recorded at  $-64^\circ$  showed disilyl sulphide to be the major silyl product. A small resonance at  $4.59 \pm 0.01$  p.p.m. assigned to dichlorosilane (literature value 4.68 p.p.m.) was also observed. This peak increased in intensity slightly as the reactants were warmed to room temperature. No evidence for any mercury-silyl derivatives could be found. In particular no mercury satellites (caused by  $^{199}\text{Hg}$ , nuclear spin of one half and natural abundance of seventeen percent) could be detected. The assignment of the resonance

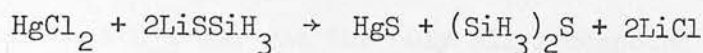
at  $5.65 \pm 0.01$  p.p.m. to disilyl sulphide was checked by H.N.S.D. of the  $^{29}\text{Si}$  satellite associated with this resonance.

$^{29}\text{Si}$  decoupling frequency observed =  $19866258 \pm 5$  Hz

$^{29}\text{Si}$  decoupling frequency required =  $19866258 \pm 5$  Hz<sup>12</sup>

### Conclusion

The reaction between lithium silyl sulphide and mercuric chloride does not produce the desired product, bis(silylthio)mercury. The major silyl product is disilyl sulphide with a small amount of dichlorosilane probably resulting from the chlorination of disilyl sulphide by mercuric chloride. The overall reaction was considered to be:



Mercuric sulphide was not identified in the reaction.

### Experiment 4.22

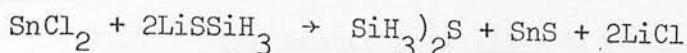
#### The reaction of stannous chloride and Lithium silyl sulphide.

The reaction between stannous chloride (0.1m moles) and lithium silyl sulphide (0.2m moles) was carried out as in experiment 4.21. The stannous chloride was prepared in the n.m.r. tube to avoid having to handle it in air or nitrogen atmospheres. A fast reaction took place at  $-64^\circ$  producing a white solid, presumed to be stannous sulphide, and the  $^1\text{H}$ -n.m.r. spectrum showed disilyl sulphide to be the only silyl compound present. On warming to  $+28^\circ$  no change in the spectrum occurred.

### Conclusion

The reaction of stannous chloride does not produce the desired product, bis(silylthio)tin. Disilyl sulphide is the major silyl product. The

overall reaction was considered to be:



Stannous sulphide was not identified in this reaction.

#### Experiment 4.23

##### The reaction of boron trichloride and lithium silyl sulphide.

Lithium silyl sulphide (0.3m moles) was prepared as usual in an ampoule fitted with a greaseless tap. Boron trichloride (0.1m moles) was added and the reaction allowed to take place in an n.m.r. tube at  $-78^\circ$ . Lithium silyl sulphide, at  $5.67 \pm 0.01$  p.p.m. and with  $^1\text{J}^{29}\text{Si-H}$  equal to  $200 \pm 1$  Hz, was the only silyl compound observed in the  $^1\text{H}$ -n.m.r. spectrum. On warming to  $-40^\circ$  a white precipitate, presumed to be lithium chloride, was formed and the resonance at 5.67 p.p.m. broadened significantly. The peak width at half height was approximately 50% greater than the natural line width as measured from the solvent resonances. A broad peak at 4.74 p.p.m. was also observed. At  $-10^\circ$  all of these resonances disappeared very quickly to give silane at  $6.80 \pm 0.01$  p.p.m. (literature 6.80 p.p.m.<sup>9</sup>) as the only observable Si-H containing product.

#### Conclusions

It is tentatively concluded that the reaction of <sup>10</sup>B of lithium silyl sulphide and boron trichloride produces boron-silyl derivatives e.g.  $\text{B}(\text{SSiH}_3)_2\text{Cl}$ . These give rise to broad n.m.r. signals caused by the quadrupolar relaxation of the  $^{11}\text{B}$  nucleus<sup>13</sup>. These derivatives decompose at  $-10^\circ$  to give silane and presumably a polymer.

Experiment 4.24The reaction of lithium silyl oxide  
and chloro trifluorosilane.

Lithium silyl oxide (0.4m moles) was prepared as described previously in an ampoule fitted with a greaseless tap. Chloro-trifluorosilane (0.4m moles) was distilled in and the reaction allowed to proceed at  $-78^{\circ}$  using diethyl ether as a solvent. A very rapid reaction took place and a white precipitate was formed. The volatile products consisted of disiloxane and a trace of silyl fluoride (0.05m mole). It was not possible to separate disiloxane from the solvent. The gas phase i.r. spectrum of the sample was consistent with only disiloxane and diethyl ether being present, after the silyl fluoride had been removed by fractionation at  $-120^{\circ}$ . The sample was also distilled into an n.m.r. tube and the  $^1\text{H}$ -n.m.r. spectrum confirmed that disiloxane was the only major silyl compound present. Weak resonances at 5.08, 5.32 and  $5.52 \pm 0.01$  p.p.m. were also observed. A rough estimate of the amount of disiloxane present could be made by comparing the intensities of the n.m.r. signal due to disiloxane and to the diethyl ether quartet, with a knowledge of the volume of the sample and density of diethyl ether. It should be stressed that this method was not accurate but it gave an estimate of between 0.1 and 0.2 m moles.

Conclusion

The reaction of lithium silyl oxide and chloro-trifluorosilane does not produce the desired product, trifluorosilyl silyl oxide. The main volatile product was disiloxane. It is interesting to note that no perfluorodisiloxane, a disproportionation product of the desired product, was detected. Indeed, it must be presumed that the  $\text{SiF}_3$



groups added must be "tied-up" in some way in the solid residue of the reaction; possibly as a polymer. No attempt was made to identify the solid formed by the reaction.

#### Experiment 4.25

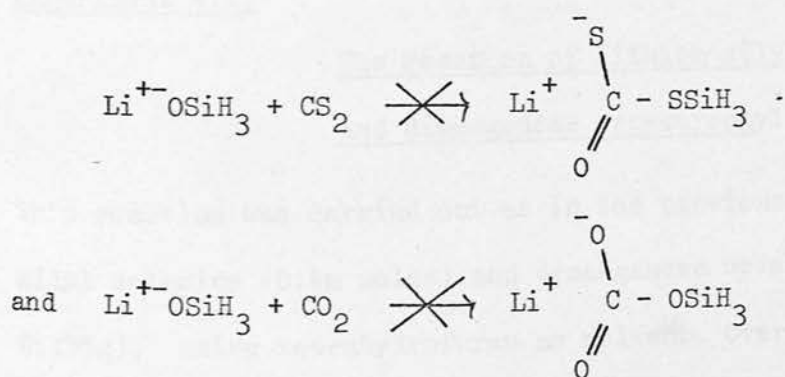
##### The reaction of lithium silyl oxide and carbon disulphide.

Lithium silyl oxide (0.3m moles) was prepared as usual and allowed to mix with carbon disulphide at room temperature in an n.m.r. tube. Diethyl ether was used as a solvent. The  $^1\text{H}$ -n.m.r. showed the silyl anion and diethyl ether to be the only proton-containing species present. After five days at room temperature the spectrum was unchanged. Furthermore the observed spectrum did not change on cooling to  $-80^\circ$ . A small amount of yellow solid was formed over the five day period, presumably caused by a partial decomposition of carbon disulphide.

A similar reaction with carbon dioxide and lithium silyl oxide was carried out and again no reaction was observed.

#### Conclusion

Under the reaction conditions quoted above, lithium silyl oxide does not undergo an insertion (or any other kind of reaction) reaction with carbon disulphide or carbon dioxide. i.e.





Experiment 4.26The reaction of lithium silyl selenide and  
manganese pentacarbonyl bromide.

Lithium silyl selenide (0.4m moles) was prepared as usual in an ampoule fitted with a greaseless tap. Using tetrahydrofuran, dried on lithium aluminium hydride, as a solvent it was allowed to react with manganese pentacarbonyl bromide (0.4m mole, 0.109 g). After two hours at room temperature, the volatile products were investigated. The main volatile product was silylmanganese-pentacarbonyl (0.23m moles, 0.053 g) identified by its i.r. spectrum<sup>14</sup>, and a trace of manganese pentacarbonyl hydride also identified by its i.r. spectrum<sup>15</sup>. No disilyl selenide or silane was observed.

Conclusion

The reaction of lithium silyl selenide and manganese pentacarbonyl bromide does not produce the desired product silylseleno manganese pentacarbonyl in high yield. Silyl manganese pentacarbonyl may well represent a decomposition product of this product. Manganese pentacarbonyl hydride is a typical decomposition product of manganese-silyl derivatives.

Experiment 4.27The reaction of lithium silyl selenide  
and dimanganese decacarbonyl

This reaction was carried out as in the previous reaction using lithium silyl selenide (0.4m moles) and dimanganese decacarbonyl (0.5m mole, 0.195g), using tetrahydrofuran as solvent. Over a period of one day no reaction was observed. Addition of trimethylsilyl chloride (0.4m mole)

gave the required amount of trimethylsilyl silyl selenide (0.3m mole) identified by its i.r. spectrum and purified by trap to trap distillation at  $-46^{\circ}$  (see chapter 3).

### Conclusion

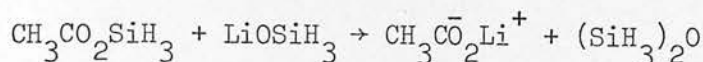
Under the conditions quoted above, lithium silyl selenide does not react with dimanganese decacarbonyl.

DISCUSSION

The preceding experiments have shown that for a given reaction, the outcome is not always predictable. Two types of reaction seem to be occurring. One is a nucleophilic substitution, e.g.



The other is a cleavage of Si-Y and Si-Z bonds by the silyl anions and other anionic species present e.g.



In any particular reaction one or both of these processes may be important. The effect of the latter process is easily demonstrated in the reactions of lithium silyl sulphide with trimethylsilyl chloride, dichloro-dimethylsilane, methyltrichlorosilane and silicon tetrachloride. Trimethylsilyl chloride gives the desired product, trimethylsilyl silyl sulphide, in high yield; dichloro-dimethylsilane gives a mixture of products, one of which is the desired product, while the others arise from the cleavage reaction; methyl-trichlorosilane and silicon tetrachloride both give the cleavage product, disilyl sulphide. Thus, as the degree of chlorination increases so does the extent of the cleavage reaction. Cleavage of Si-H bonds appear to be a minor type of reaction for the silyl anions.

Although only a relatively small number of reactions have been attempted it is still obvious that the cleavage of desired products by a local excess of silyl anion represents a serious problem. The following two sections are an attempt to deal with this problem.

## PART B

### Some Reactions of Group V and Group VI

#### silyl anions with closely related Molecules

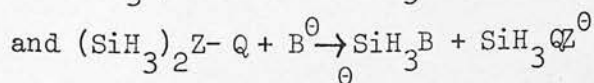
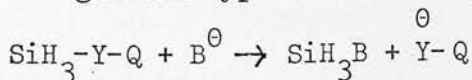
# INTRODUCTION

During the course of this work the following observations have been made.

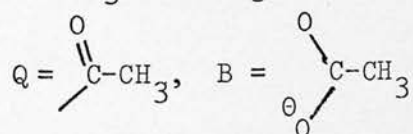
1. Species of the form  $\text{Li Y}(\text{SiH}_3)$  and  $\text{Li Z}(\text{SiH}_3)_2$  ( $\text{Y} = \text{O}, \text{S}, \text{Se}; \text{Z} = \text{P}, \text{As}$ ) can be prepared in high yield by the cleavage of the Si-Y and S-Z bonds in  $(\text{SiH}_3)_2\text{Y}$  and  $(\text{SiH}_3)_3\text{Z}$  by methyl lithium.
2. A major side-reaction of the silyl anions produces  $(\text{SiH}_3)_2\text{Y}$  and  $(\text{SiH}_3)_3\text{Z}$ . It has been postulated that it occurs by the cleavage of the new Si-Y and Si-Z bond in the product by a local excess of the reactant silyl anion.
3. In the preparation and reactions of the silyl anions it is very unusual to observe significant quantities of silane or hydrogen. These are the usual products of the decomposition of silyl compounds.

The above observations point to a facile cleavage of Si-Y and Si-Z bonds by strong bases. It is not unusual for silicon hydrides to react with strong bases but it is usual for massive decomposition to hydrogen, silane and polymeric species to take place (see chapter 3 for a fuller discussion). This is evidently not occurring in the reactions and preparations of the silyl anions.

The general type of reaction postulated is:-



e.g.  $\text{Q} = \text{SiH}_3, \text{B} = \text{CH}_3$



The following series of experiments were initiated in an attempt to investigate the above reaction using closely related molecules. One

should notice that when Q is  $\text{SiH}_3$  and B is  $\text{YSiH}_3$  or  $\text{Z}(\text{SiH}_3)_2$  then there is a possibility of chemical exchange. Nuclear magnetic resonance spectroscopy is the best technique for studying this type of process and this was indeed the method used. This method is particularly useful in that rough estimates of reaction rates can be made. For an exchanging system, as observed by n.m.r., at coalescence the relationship shown below is valid.

$$T\Delta\nu = \frac{1}{2\pi}^{16}$$

T = lifetime of the exchange site

(measured in seconds)

$\Delta\nu$  = frequency difference between the  
discrete signals

(measured in hertz)

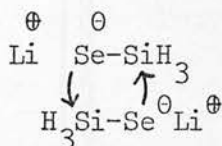
In the region of fast exchange T is less than  $\frac{1}{2\pi\Delta\nu}$  (see appendix 2 for a fuller discussion).



Experiment 4.28The Reaction of lithium silyl selenide  
and lithium silyl selenide

It may seem strange to consider this as a reaction but the fact remains that lithium silyl selenide in diethyl ether does not show  $^{77}\text{Se}$  satellites at temperatures above  $-20^{\circ}$ . This can only be explained in terms of an exchange process occurring at a rate fast on the n.m.r. time scale at temperatures above  $-20^{\circ}$ . The process must involve the cleavage of Si-Se bonds since Si-Se coupling is destroyed (see figure 4.1)

The simplest possible explanation would be a four centre type of reaction



The lifetime of a Si-Se bond in lithium silyl selenide at approximately  $-20^{\circ}$  must be of the order of 0.014 seconds.

It seems probable that lithium silyl oxide and lithium silyl sulphide will undergo similar exchange processes, probably at reduced rates. It is not possible to show this using common  $^1\text{H}$ -n.m.r. techniques.

Experiment 4.29The Reaction of lithium silyl oxide and  
disiloxane.

Lithium silyl oxide (0.2m moles) was added to disiloxane (0.2m moles) in an n.m.r. tube, using diethyl ether as a solvent. A clear solution resulted and the  $^1\text{H}$ -n.m.r. spectrum showed two discrete signals (in the intensity ratio of 1:2) assigned to the starting materials.

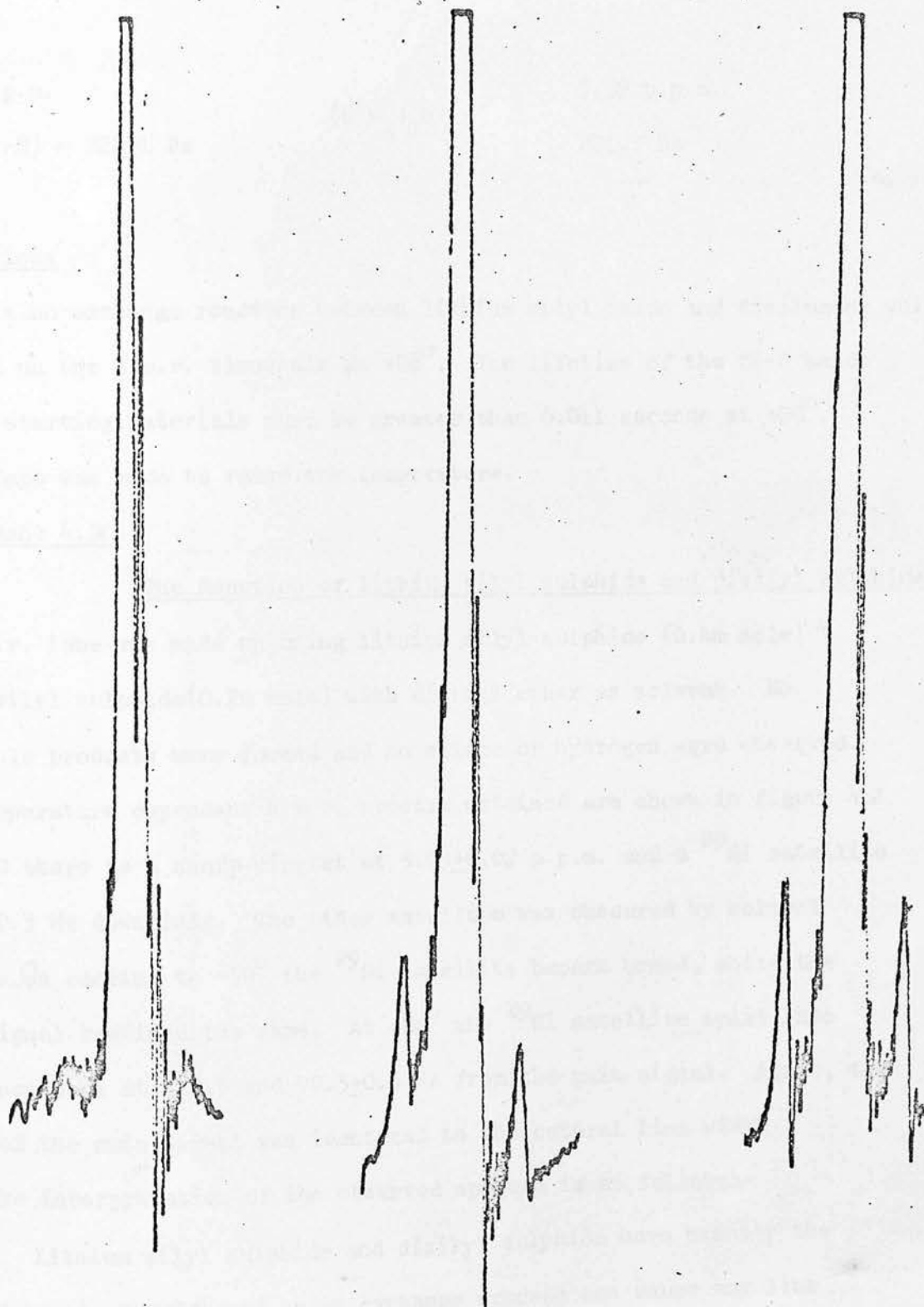
FIGURE 4.1

$^1\text{H}$  NMR SPECTRUM OF  $[\text{SiH}_3\text{Se}] \text{Li}$  in  $\text{Et}_2\text{O}$

-  $10^\circ$

-  $20^\circ$

-  $30^\circ$



<u>Observed Signals</u>	<u>Assignment</u>	<u>Literature</u>
5.25±0.02 p.p.m. $^1J(^{29}\text{Si-H}) = 194 \pm 1 \text{ Hz}$	$\text{LiOSiH}_3$	5.25 p.p.m. 194 Hz
5.39 p.p.m. $^1J(^{29}\text{Si-H}) = 222 \pm 1 \text{ Hz}$	$(\text{SiH}_3)_2\text{O}$	5.39 p.p.m. <sup>2</sup> 221.5 Hz

### Conclusions

There is no exchange reaction between lithium silyl oxide and disiloxane which is fast on the n.m.r. timescale at +28°. The lifetime of the Si-O bonds in the starting materials must be greater than 0.011 seconds at +28°.

No attempt was made to raise the temperature.

### Experiment 4.30

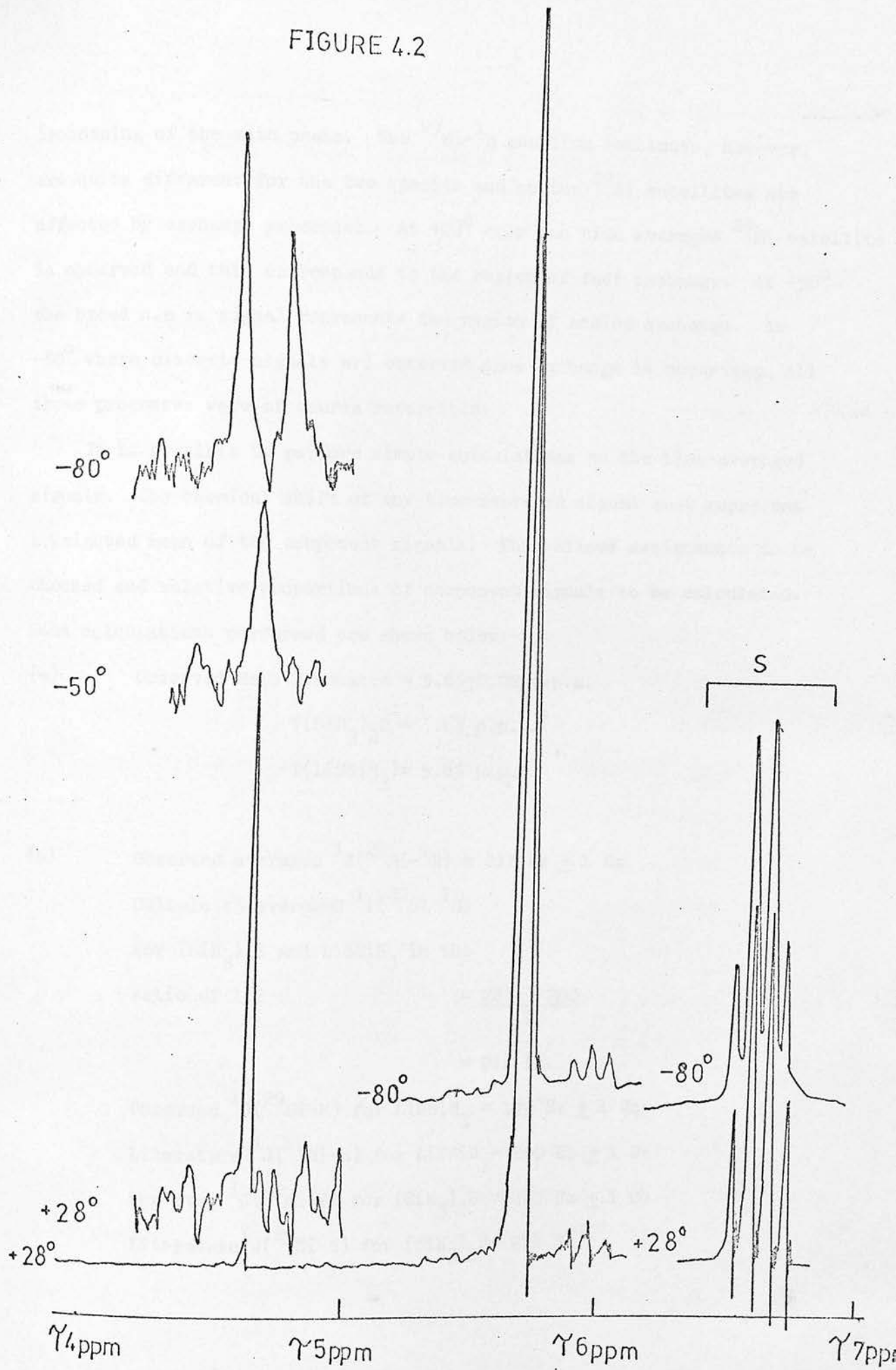
#### The Reaction of lithium silyl sulphide and disilyl sulphide.

An n.m.r. tube was made up using lithium silyl sulphide (0.4m mole) and disilyl sulphide (0.2m mole) with diethyl ether as solvent. No insoluble products were formed and no silane or hydrogen were observed. The temperature dependent n.m.r. spectra obtained are shown in figure 4.2 at 28°C there is a sharp singlet at 5.65±0.02 p.p.m. and a  $^{29}\text{Si}$  satellite 105.5±0.5 Hz downfield. The other satellite was obscured by solvent signals. On cooling to -50° the  $^{29}\text{Si}$  satellite became broad, while the main signal remained the same. At -80° the  $^{29}\text{Si}$  satellite split into two resonances at 112.5 and 99.5±0.5 Hz from the main signal. Again, the width of the main signal was identical to the natural line width.

The interpretation of the observed spectra is as follows:-

Lithium silyl sulphide and disilyl sulphide have exactly the same  $^1\text{H}$  chemical shift and so no exchange process can cause any line

FIGURE 4.2



broadening of the main peaks. The  $^{29}\text{Si}-^1\text{H}$  coupling constants, however, are quite different for the two species and so the  $^{29}\text{Si}$  satellites are affected by exchange processes. At  $+28^\circ$  only one time averaged  $^{29}\text{Si}$  satellite is observed and this corresponds to the region of fast exchange. At  $-50^\circ$  the broad n.m.r. signal represents the region of medium exchange. At  $-80^\circ$  where discrete signals are observed slow exchange is occurring. All these processes were of course reversible.

It is possible to perform simple calculations on the time-averaged signals. The chemical shift of any time-averaged signal must represent a weighted mean of the component signals. This allows assignments to be checked and relative proportions of component signals to be calculated. Some calculations performed are shown below:-

(a) Observed Main Resonance =  $5.65 \pm 0.02$  p.p.m.

$$\tau(\text{SiH}_3)_2\text{S} = 5.65 \text{ p.p.m.}^9$$

$$\tau(\text{LiSSiH}_3) = 5.65 \text{ p.p.m.}$$

(b) Observed averaged  $^1J(^{29}\text{Si}-^1\text{H}) = 211 \text{ Hz} \pm 1 \text{ Hz}$

Calculated averaged  $^1J(^{29}\text{Si}-^1\text{H})$

for  $(\text{SiH}_3)_2\text{S}$  and  $\text{LiSSiH}_3$  in the

$$\text{ratio of } 1:2 = \frac{224 + 200}{2}$$

$$= 212 \text{ Hz.}$$

Observed  $^1J(^{29}\text{Si}-\text{H})$  for  $\text{LiSSiH}_3 = 199 \text{ Hz} \pm 1 \text{ Hz}$

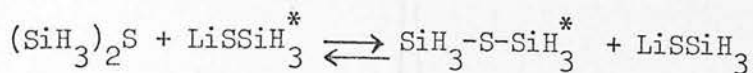
Literature  $^1J(^{29}\text{Si}-\text{H})$  for  $\text{LiSSiH}_3 = 200 \text{ Hz} \pm 1 \text{ Hz}$

Observed  $^1J(^{29}\text{Si}-\text{H})$  for  $(\text{SiH}_3)_2\text{S} = 225 \text{ Hz} \pm 1 \text{ Hz}$

Literature  $^1J(^{29}\text{Si}-\text{H})$  for  $(\text{SiH}_3)_2\text{S} = 224 \text{ Hz}^2$

## Conclusions

There is an exchange process taking place described by the equation



$\text{SiH}_3^*$  - represents an  $\text{SiH}_3$  group which has its environment changed by the reaction. At  $+28^\circ$  this reaction is fast on the n.m.r. timescale. At  $-50^\circ$  it is medium and at  $-80^\circ$  it is slow. The lifetime of a Si-S bond at  $-50^\circ$  is of the order of 0.013 seconds.

## Experiment 4.31

### The reaction of disilylselenide and lithium silyl selenide

Lithium silyl selenide (0.2m mole) and disilyl selenide (0.2 m mole) were allowed to react in an n.m.r. tube with diethyl ether as solvent. A clear solution resulted. No silane or hydrogen was formed. The temperature dependent n.m.r. spectra obtained are shown in figure 4.3. At  $+28^\circ$  a sharp singlet at  $5.97 \pm 0.02$  p.p.m. was observed. Associated with this signal was a  $^{29}\text{Si}$  satellite  $108 \pm 0.5$  Hz downfield. On cooling to  $-80^\circ$  very little change was observed. The main signal showed signs of broadening but viscosity effects prevented further cooling of the sample.

As in the previous experiment some simple calculations were done.

They are shown below

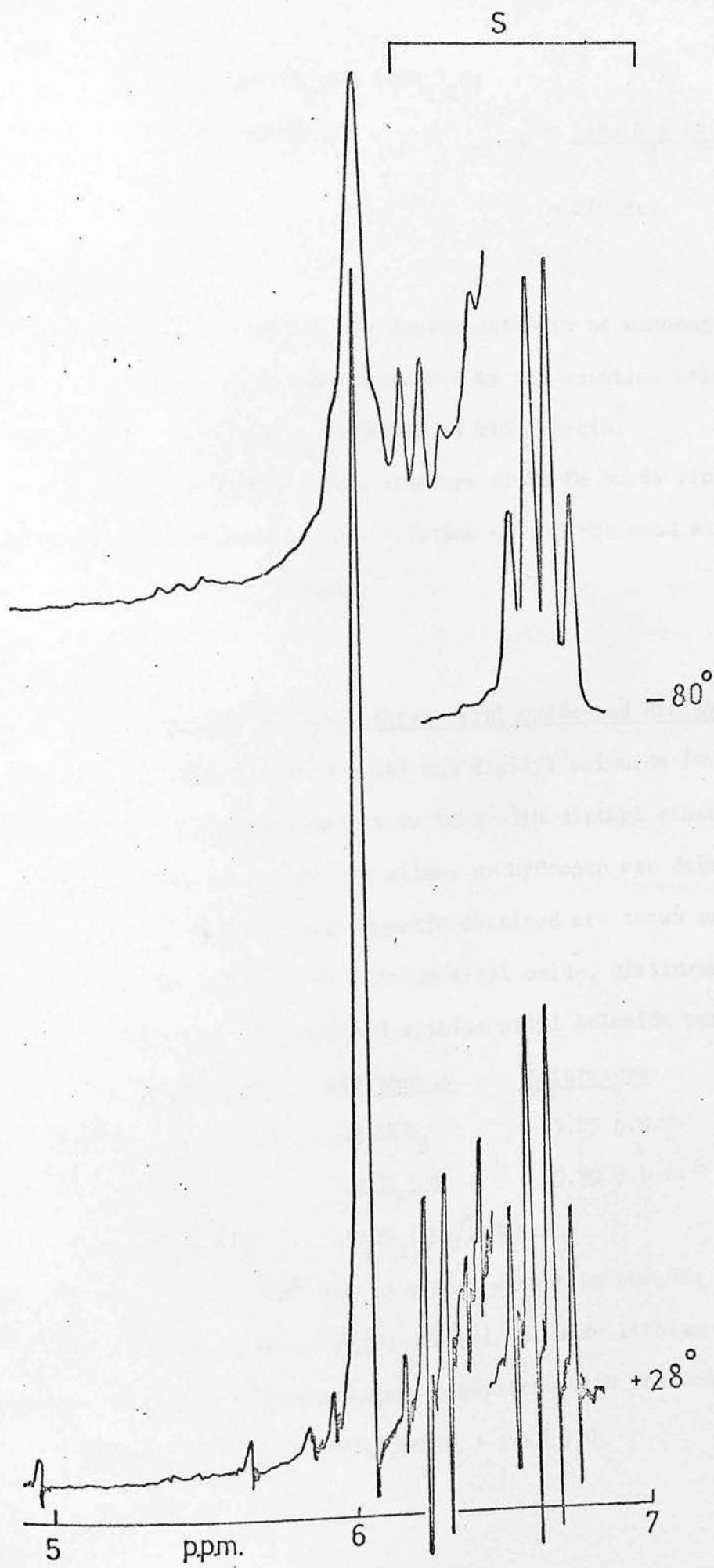
$$\begin{aligned} \text{(a)} \quad \text{Observed averaged chemical shift} &= 5.97 \pm 0.02 \text{ p.p.m.} \\ \text{Calculated averaged chemical shift} &= \frac{(5.88 \times 2 + 6.06)}{3} \text{ p.p.m.} \\ &= 5.94 \text{ p.p.m.} \end{aligned}$$

It should be noted that chemical shifts are not reliable since they are usually a function of temperature. This does not apply to the same extent to coupling constants.

$$\begin{aligned} \text{(b)} \quad \text{Observed averaged } {}^1\text{J}({}^{29}\text{Si}-{}^1\text{H}) &= 216 \pm 1 \text{ Hz} \\ \text{Calculated average } {}^1\text{J}({}^{29}\text{Si}-{}^1\text{H}) & \end{aligned}$$



FIGURE 4.3



for  $\text{LiSeSiH}_3$  and  $(\text{SiH}_3)_2\text{Se}$

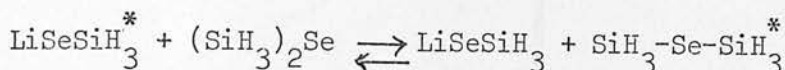
in the ratio 1:1

$$= \frac{198 \times (2 \times 225)}{3} \text{ Hz}$$

$$= 216 \text{ Hz.}$$

### Conclusions

The observed n.m.r. spectra are consistent with an exchange process fast on the n.m.r. timescale described by the equation below.



This process must involve fast cleavage of Si-Se bonds since no  $^{77}\text{Se}$  satellites were observed. The lifetime of a Si-Se bond at  $-80^\circ$  cannot be greater than 0.011 seconds.

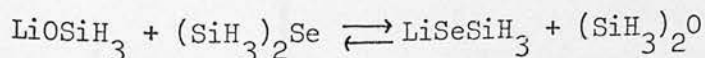
### Experiment 4.32

#### The reaction of lithium silyl oxide and disilyl selenide

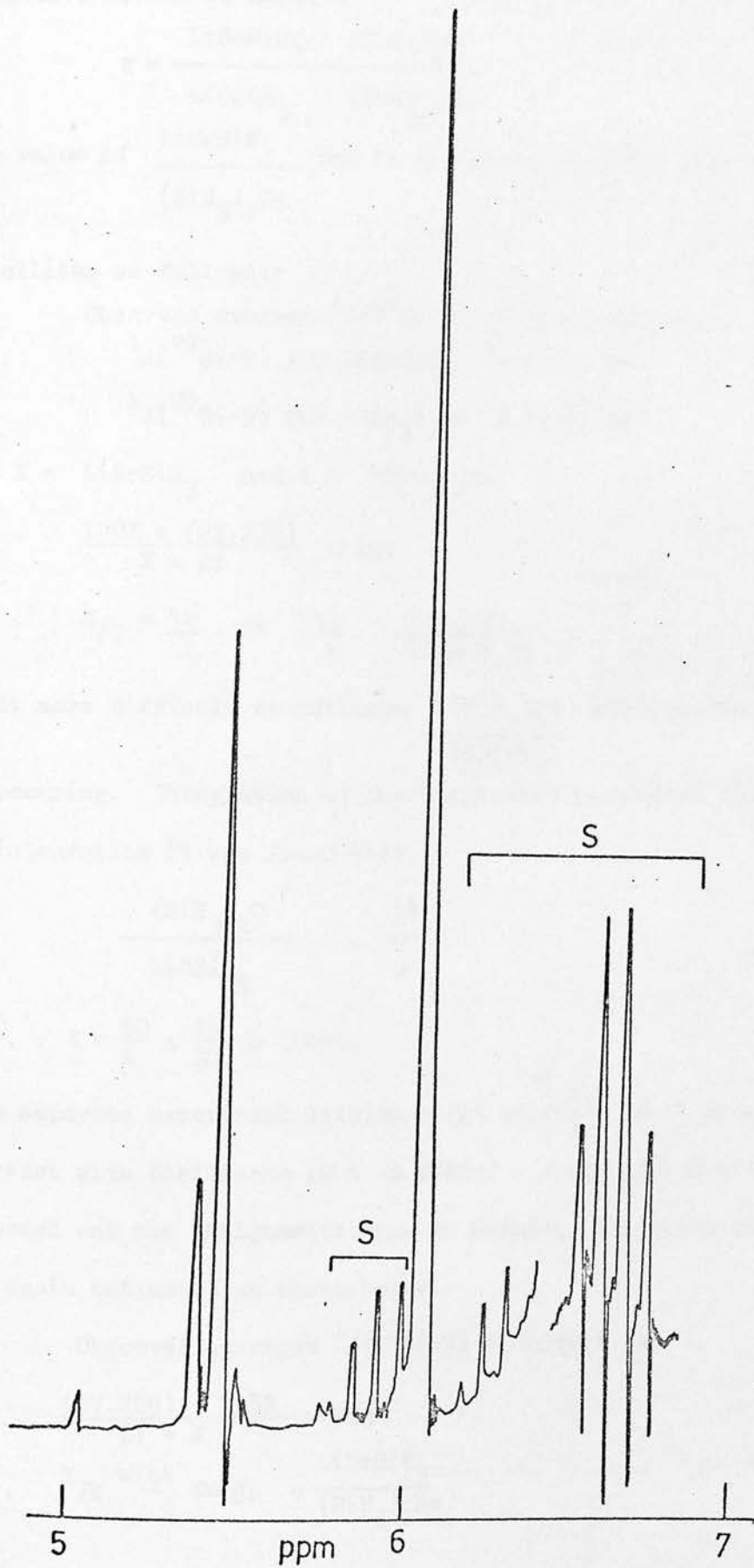
Lithium silyl oxide (0.4 m mole) and disilyl selenide (0.2 m.mole) were allowed to react in an n.m.r. tube with diethyl ether as solvent. A clear solution resulted. No silane or hydrogen was detected. The temperature dependent n.m.r. spectra obtained are shown on Figure 4.4. At  $+28^\circ$  signals assigned to lithium silyl oxide, disiloxane and time averaged disilyl selenide and lithium silyl selenide were observed.

<u>Observed Signals</u>	<u>Assignment</u>	<u>Literature</u>
5.25 $\pm$ 0.02 p.p.m.	$\text{LiOSiH}_3$	5.25 p.p.m.
5.40 $\pm$ 0.02 p.p.m.	$(\text{SiH}_3)_2\text{O}$	5.39 p.p.m. <sup>9</sup>
6.05 $\pm$ 0.02 p.p.m.	$(\text{SiH}_3)_2\text{Se/LiSeSiH}_3$	-

Cooling the tube to  $-60^\circ$  had no effect except to broaden the signal assigned to the time averaged disilyl selenide lithium silyl selenide signal. The observed spectra are consistent with the following reaction.



190.  
FIGURE 4.4



If it is assumed that the reaction is at equilibrium then an equilibrium constant, K, can be defined

$$K = \frac{\text{LiSeSiH}_3 \quad (\text{SiH}_3)_2^0}{\text{LiOSiH}_3 \quad (\text{SiH}_3)_2\text{Se}}$$

The value of  $\frac{\text{LiSeSiH}_3}{(\text{SiH}_3)_2\text{Se}}$  can be estimated from the time averaged  $^{29}\text{Si}$

satellites as follows:-

$$\text{Observed average } {}^1J(^{29}\text{Si-H}) = 199 \text{ Hz} \pm 0.5 \text{ Hz}$$

$${}^1J(^{29}\text{Si-H}) \text{ for } \text{LiSeSiH}_3 = 198 \pm 1 \text{ Hz}$$

$${}^1J(^{29}\text{Si-H}) \text{ for } (\text{SiH}_3)_2\text{Se} = 225 \pm 1 \text{ Hz}^2$$

Let  $X = \text{LiSeSiH}_3$  and  $Y = (\text{SiH}_3)_2\text{Se}$

$$\therefore \frac{198X + (2Y \cdot 225)}{X + 2Y} = 199$$

$$\therefore X/Y = \frac{52}{1} \approx \frac{50}{1} = \frac{\text{LiSeSiH}_3}{(\text{SiH}_3)_2\text{Se}}$$

It is more difficult to estimate  $\frac{(\text{SiH}_3)_2^0}{\text{LiOSiH}_3}$  since no fast exchange process

is occurring. Integration of the respective resonances had to be resorted to.

By integration it was found that,

$$\frac{(\text{SiH}_3)_2^0}{\text{LiOSiH}_3} = \frac{54}{30}$$

$$\therefore K = \frac{50}{1} \times \frac{54}{30} \approx 100 \pm 20$$

In a separate experiment lithium silyl selenide (0.2 m moles) was allowed to react with disiloxane (0.4 m moles) a very similar spectrum was recorded and the assignments were as before. The equilibrium constant was again estimated as shown below.

$$\text{Observed averaged } {}^1J(^{29}\text{Si-H}) = 203 \pm 0.5 \text{ Hz}$$

$$\therefore \frac{(2Y \cdot 225) + 198X}{2Y + X} = 203$$

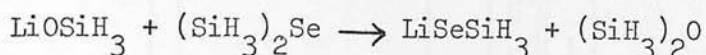
$$\therefore X/Y = \frac{44}{5} \approx 9 = \frac{\text{LiSeSiH}_3}{(\text{SiH}_3)_2\text{Se}}$$

The value of  $\frac{(\text{SiH}_3)_2\text{O}}{\text{LiOSiH}_3}$  was again estimated by integration and a value of  $9/1$  was obtained.

$$\therefore K = 9 \times 9/1 = 80 \quad 100 \pm 20$$

### Conclusions

These two experiments imply that in each case the system was at equilibrium and although the values of  $K$  are only rough estimates they agree within the error that the equilibrium lies far to the right for the reaction



This reaction is slow on the n.m.r. timescale. It would appear that reactions involving oxygen are slow on the n.m.r. timescale while those involving selenium are fast. As usual no Si-H bond cleavage was detected since no silane or hydrogen was observed.

### Experiment 4.33

#### The reaction of lithium silyl sulphide and disilyl selenide

Lithium silyl sulphide (0.2 m mole) and disilyl selenide (0.2m moles) were allowed to react in an n.m.r. tube with diethyl ether as solvent. The  $^1\text{H}$ -n.m.r. spectrum observed at  $+28^\circ$  showed only one signal at  $5.83 \pm 0.02$  p.p.m. and a  $^{29}\text{Si}$  satellite associated with it  $108 \pm 0.5$  Hz downfield. The other satellite was obscured by solvent signals. The main signal broadened slowly with decreasing temperature until at  $-85^\circ$  two broad main peaks were observed at  $5.70 \pm 0.05$  p.p.m. and  $6.08 \pm 0.05$  p.p.m. (see figure 4.5) These peaks were in the approximate ratio of 2:1 and had  $^{29}\text{Si}$  satellites associated with them. The values of  $^1J(^{29}\text{Si-H})$  were  $192 \pm 5$  Hz and  $224 \pm 5$  Hz respectively. This is consistent with the assignment of the peaks to lithium silyl selenide and disilyl sulphide. Table 4.2 shows some of the line widths measured at various temperatures.

FIGURE 4.5

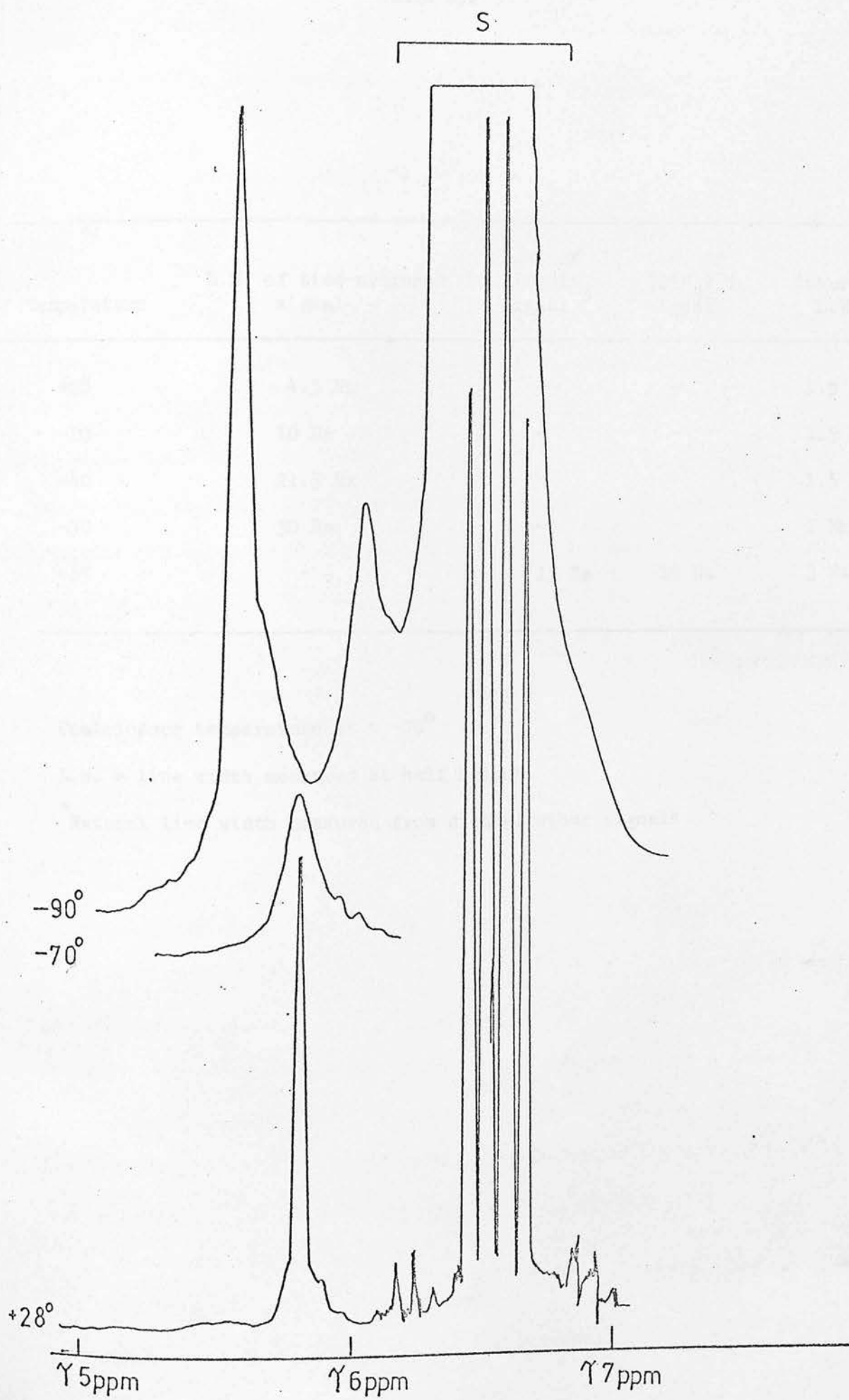




Table 4.2

Temperature	L.W. of time-averaged signal	L.W. of LiSeSiH <sub>3</sub> Signal	L.W. of (SiH <sub>3</sub> ) <sub>2</sub> S signal	Natural L.W.*
+28	4.5 Hz	-	-	1.5 Hz
-10	10 Hz	-	-	1.5 Hz
-40	21.5 Hz	-	-	1.5 Hz
-50	30 Hz	-	-	2 Hz
-85	-	15 Hz	15 Hz	3 Hz

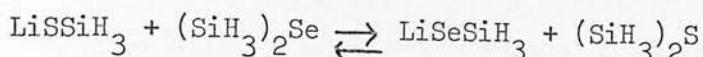
Coalescence temperature at  $\sim -70^{\circ}$

L.W. = line width measured at half height

\* Natural line width measured from diethyl ether signals

## Conclusions

The observations made are consistent with the following reaction taking place



at  $-85^\circ$  this reaction lies far to the right. To confirm this, disilyl sulphide (0.2m mole) and lithium silyl selenide (0.2m mole) were allowed to react in an n.m.r. tube. The spectrum was identical to the one already obtained. This implies that the reaction is at equilibrium and that it must involve the cleavage of Si-S and Si-Se bonds. It is also reasonable to assume that since the reaction rate for this reaction is relatively insensitive to temperature the activation energy is low. As with the previous reactions no Si-H cleavage occurs.

## Note

It would be relevant to consider the product distribution of the above reaction at room temperature. Unfortunately it is not possible to determine this, as the following attempts show.

### (a) The use of $^{29}\text{Si-H}$ , coupling constants

Observed  $^1J(^{29}\text{Si-H})$  at  $28^\circ\text{C}$  =  $216 \pm 1$  Hz

for  $\text{LiSeSiH}_3 + (\text{SiH}_3)_2\text{S}$  the

calculated value = 215.3 Hz

for  $\text{LiSSiH}_3 + (\text{SiH}_3)_2\text{Se}$ , the

calculated value = 216.6 Hz

Therefore any value of the equilibrium constant would give a value of  $^1J(^{29}\text{Si-H})$  which would lie within the experimental error. Variation of the concentrations of starting material would not help either.

### (b) The use of $^{29}\text{Si}$ frequencies in a H.N.S.D. experiment

Observed frequency required to

decouple averaged  $^{29}\text{Si}$  satellite

at  $28^\circ$

= 19866090 Hz

Decoupling was still effective at  $\pm 100$  Hz from this frequency.

$$\text{Weighted average of } (\text{SiH}_3)_2\text{S} + \text{LiSeSiH}_3 = \frac{(19866258 \times 2) + 19865763}{3}$$

$$= 19866093 \text{ Hz}$$

$$\text{Weighted average of } (\text{SiH}_3)_2\text{Se} + \text{LiSSiH}_3 = \frac{(19866025 \times 2) + 19866025}{3}$$

$$= 19866025 \text{ Hz.}$$

Again  $^{29}\text{Si}$  decoupling does not appear to be of any real use. The  $^{29}\text{Si}$  spectrum itself must be broad at  $+28^\circ$  as witnessed by the H.N.S.D. experiment. It is tentatively suggested that because the frequency that produces maximum decoupling of the  $^{29}\text{Si}$  satellites corresponds to the average of disilyl sulphide and lithium silyl selenide then these species are indeed present to a larger extent than the other products. It should be emphasised that by the very nature of the H.N.S.D. experiment, using a time averaged signal is not a reliable method. For example, the  $^{29}\text{Si}$  spectrum should be resolved at a higher temperature than the  $^1\text{H}$  spectrum. Therefore, at  $-40^\circ$  for example, decoupling of the  $^1\text{H}$  signal should lead to the detection of disilyl sulphide, disilyl selenide, lithium silyl selenide and lithium silyl sulphide if they are present. Unfortunately, they would have to be present in a fairly large proportion of the mixture before any significant collapse of the  $^{29}\text{Si}$  satellite observed in the  $^1\text{H}$  spectrum would be detected. The real answer would be to run a temperature dependent  $^{29}\text{Si}$  spectrum directly.

(c) The use of chemical shifts

$$\text{Average chemical shift of } \text{LiSSiH}_3 + (\text{SiH}_3)_2\text{Se} = \frac{5.65 + (5.88 \times 2)}{3}$$

$$= 5.80 \text{ p.p.m.}$$

$$\text{Averaged chemical shift of } \text{LiSeSiH}_3 + (\text{SiH}_3)_2\text{S} = \frac{6.06 + (5.65 \times 2)}{3}$$

$$= 5.79 \text{ p.p.m.}$$

Observed value

$$= 5.83 \pm 0.02 \text{ p.p.m.}$$

Again, any value of the equilibrium constant would give a value of the average chemical shift that would lie within the experimental error.

(d) Analysis of the products of the reaction

Opening up the n.m.r. tube at  $28^{\circ}$  and analysing the product would not be of any real value since there would always be the possibility that the equilibrium had been disturbed.

Experiment 4.34

The reaction of trisilylphosphine and lithium disilyl phosphide

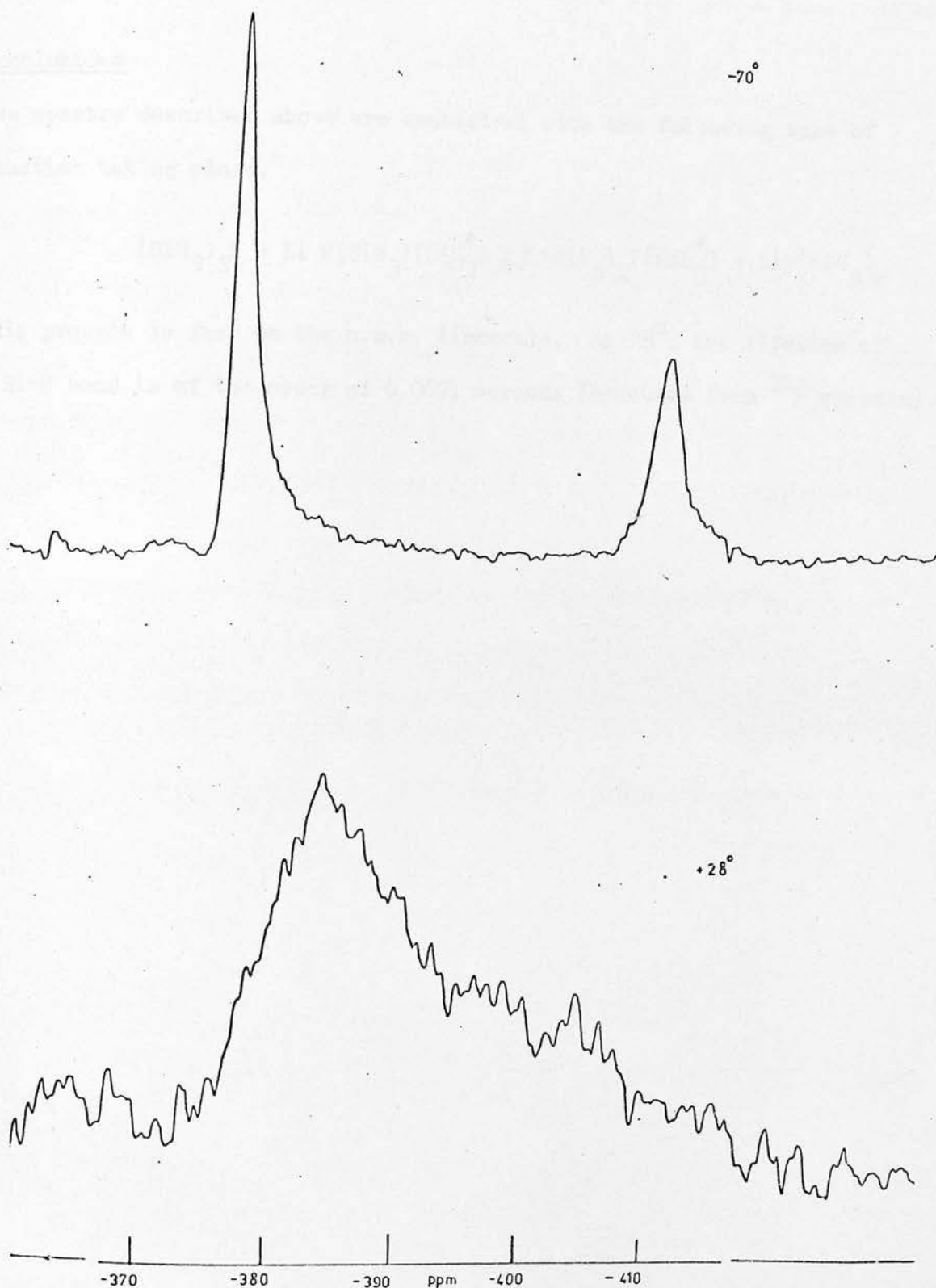
An n.m.r. tube containing trisilyl phosphine (1.5m mole) and lithium disilyl phosphide (0.2m mole) was made up as before. No insoluble material was observed and no hydrogen or silane.

The  $^1\text{H}$ -n.m.r. spectrum showed a broad line at  $6.05 \pm 0.02$  p.p.m. On cooling down the tube to  $-80^{\circ}$  this resonance was virtually unchanged. These observations are consistent with a fast exchange process producing a time averaged signal with a lifetime of approximately less than 0.007 seconds for a P-Si bond at  $-80^{\circ}$ .

A  $^{31}\text{P}$ -n.m.r. spectrum was also run. This showed a very broad line at  $28^{\circ}\text{C}$  (line width = 600 Hz) centred at -382 p.p.m. On cooling to  $-70^{\circ}$  this resolved into two peaks at -377.8 p.p.m. and -410.5 p.p.m. (see figure 4.6) These were assigned to trisilylphosphine (literature -373 p.p.m.) and lithium disilyl phosphide (literature - 406 p.p.m.) small discrepancies of  $\delta^{31}\text{P}$  are probably due to solvent or temperature effects. The process was of course reversible.

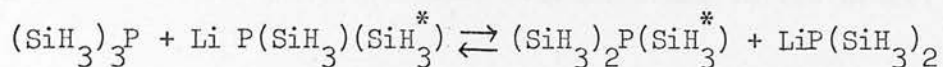
The spectra described above were recorded while noise decoupling protons, as is normal for  $^{31}\text{P}$  spectra. Exactly the same spectra were observed when no proton noise decoupling was applied. This must mean that the exchange reaction decouples protons. This is exactly what one would expect.

FIGURE 4.6



### Conclusions

The spectra described above are consistent with the following type of reaction taking place.

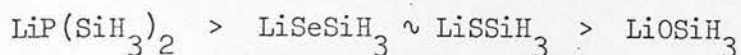


This process is fast on the n.m.r. timescale. At 28°C the lifetime of a Si-P bond is of the order of 0.0001 seconds (measured from  $^{31}\text{P}$  spectra).



### DISCUSSION

The preceeding experiments show that bond cleavage is a facile process for the silyl anions. The rates of these reactions are in the order.



Care should be taken since these processes have been shown to be concentration dependent but the order of rates is probably quite accurate. Since the experiments were all done at similar concentrations of reactants.

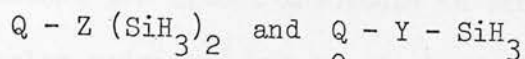
Although this study is limited to closely related systems it is almost certainly true that this is a general type of reaction. The next section deals with attempts to reduce the effectiveness of this reaction.

## PART C

### Attempts to modify the reactivity of the silyl anions of group V and VI

INTRODUCTION

The reactions of the silyl anions of group V and VI described in part A of this chapter represent an attempt to synthesise derivatives of the type



(Q = any group of interest e.g.  $CH_3-C \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} O \\ \end{smallmatrix}$ , and Z = P, Y = O, S, Se)

In a large number of cases the main volatile product was  $(SiH_3)_3Z$  or  $(SiH_3)_2Y$  and the desired products were not observed. The implication of the formation of  $(SiH_3)_3Z$  and  $(SiH_3)_2Y$  is that either a disproportionation of the desired product is taking place or that it is being attacked by a local excess of the silyl anion. It is well known that some group V and VI silyl derivatives disproportionate readily, especially in the liquid phase, and it has been shown that silyl anions undergo rapid cleavage reactions. Thus, both of these processes can occur and in some cases they may be important. It is not unreasonable to suggest that the silyl anion could even catalyse the disproportionation.

Unfortunately there is very little that can be done with a compound that is not stable to disproportionation if one wants to handle it, at room temperature, in a vacuum line. The problem is even more acute if the compound exists as a solid or liquid at room temperature. No real attempt to limit decomposition by disproportionation was made. Attempts to limit the extent to which decomposition was caused by cleavage reactions by a local excess of silyl anion fell into three distinct categories. The first was to use benzene as a solvent instead of diethyl ether. The second was

to use trimethylamine in the reactions and the third was to carry out reactions in the absence of solvent. In all three cases the reactions were carried out at as low a temperature as possible.

The rationale behind each approach is as follows:-

(1) The use of benzene as a solvent

The silyl anions are almost insoluble in benzene (and probably in most other non-polar solvents) but the desired products would almost certainly be soluble in benzene. This could afford a method of isolating reaction products from a local excess of the silyl anions. It is hoped that the main reaction would take place at the surface of the silyl anion and that the product would quickly diffuse into the benzene and so be safe from any further reaction.

(2) The use of trimethylamine

It is well known that alkyl lithium reagents are associated in solution<sup>19</sup>; for instance methyl lithium is a tetramer in diethyl ether. It does not seem unreasonable to expect that lithium silyl anions of group V and VI would be associated as well, even though the analogy is not strictly valid. Cluster formation would lead to local high concentrations of the silyl anion and hence give a higher probability of side reactions occurring. It would also make the system relatively insensitive to dilution. It is well known that tertiary amines give complexes with alkyl lithium compounds that are monomers<sup>19</sup>, such as that formed by tetramethyl ethylenediamine and n-butyl lithium. Again with the usual reservations about the validity of the comparison, the interaction of trimethylamine and the silyl anions was investigated.

(3) The absence of solvent

The logic behind this approach is essentially the same as

that of using benzene. The main advantage of working without solvent is that a large surface area of solid silyl anion can be presented to the reactant. If all of the anion reacts at approximately the same time then this will reduce the possibility of side reactions occurring.

Each of these approaches was investigated to such an extent that its usefulness could be assessed. Details are given in the following pages.

Experiment 4.35The  $^1\text{H}$ -n.m.r. spectrum of lithium silyl selenide in benzene.

Lithium silyl selenide (0.2m moles) was prepared in an n.m.r. tube on the vacuum line in diethyl ether. The excess of solvent was pumped off over a period of several hours. Dry, degassed benzene was then distilled onto the solid and the tube sealed off. On standing at room temperature for several hours no appreciable quantity of the anion appeared to dissolve in the benzene.

The proton n.m.r. spectrum showed, besides peaks due to benzene, a very small amount of residual diethyl ether and nothing else.

Conclusion

Lithium silyl selenide does not dissolve to any appreciable extent in benzene. It should be noted that n.m.r. spectroscopy is not a particularly sensitive technique and small quantities of the anion ( $<0.01$  m mole in 2 ml of benzene) could be present and not detected.

Experiment 4.36Introduction

It has been shown that small amounts of lithium silyl selenide in disilyl selenide will cause the  $^{77}\text{Se}$  satellites of disilyl selenide to collapse and also cause a change in  $^1\text{J}(^{29}\text{Si-H})$  proportional to the amount of lithium silyl selenide present. This behaviour has been interpreted as involving fast cleavage of Si-Se bonds and indeed this is a likely mechanism for side reactions of the anion.

Lithium silyl selenide (0.2m moles) was prepared in an n.m.r. tube as before and after the solvent was removed, disilyl selenide



0.2m moles) and benzene were added. As before, the solid anion did not appear to dissolve.

The  $^1\text{H}$ -n.m.r. spectrum showed only disilyl selenide and a small amount of residual diethyl ether. The n.m.r. parameters for disilyl selenide were normal. i.e.  $^1\text{J}(^{29}\text{Si-H}) = 225 \pm 1$  Hz,  $\text{TSiH} = 6.11 \pm 0.02$  p.p.m.  $^2\text{J}(^{77}\text{Se-SiH}) = 15 \pm 1$  Hz.

Although the  $^{77}\text{Se}$  satellites appeared slightly broadened this could well have been due to lack of homogeneity in the magnetic field caused by large quantities of solid in the tube.

### Conclusion

Lithium silyl selenide does not dissolve appreciably in benzene even if disilyl selenide is present. Also the intensity of the signal observed for disilyl selenide was consistent with a concentration of  $0.2 \text{ mmole m}^{-3}$  and so there is no strong interaction between lithium silyl selenide and disilyl selenide.

### Experiment 4.37

The reaction of methyl iodide and lithium  
silyl selenide in benzene.

### Introduction

It has been shown that methyl iodide reacts cleanly with lithium silyl selenide in diethyl ether solution (Experiment 4.1). Thus it constitutes a good test of the usefulness of benzene as a reaction medium.

### Experimental

Methyl iodide (0.5m mole) was added to lithium silyl selenide (0.3m mole) prepared in an n.m.r. tube as before, and benzene

(approximately 2 mls) added. After sealing off the tube and allowing the reactants to warm to room temperature, the <sup>1</sup>H-n.m.r. spectrum was recorded. This showed the presence of methyl silyl selenide, the excess of methyl iodide and a small amount of disilyl selenide (5% of Si-H based on relative peak heights).

### Conclusion

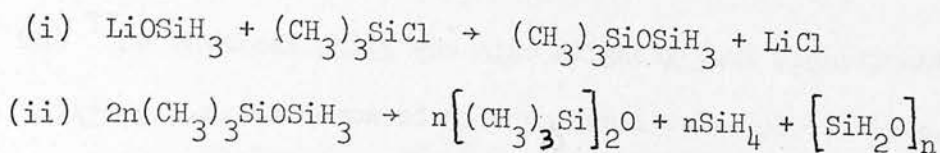
Reaction of lithium silyl selenide and methyl iodide is possible, in the absence of diethyl ether, in benzene. The yield of disilyl selenide is very low but comparable to that when the reaction is done in diethyl ether (usually about 5% based on total Si-H).

### Experiment 4.38

#### The reaction of lithium silyl oxide and trimethylsilyl chloride in benzene

### Introduction

The reaction of lithium silyl oxide (0.3m mole) and trimethylsilyl chloride (0.3m mole) was carried out, using diethyl ether as a solvent, in an ampoule fitted with a greaseless tap. A fast reaction took place at room temperature forming a white precipitate. The volatile products consisted of silane (0.2m mole) and hexamethyl disiloxane (0.2m mole) separated by trap to trap distillation at  $-64^{\circ}$ . No disiloxane was detected but a trace of a silyl-oxygen derivative was detected. All products were identified by their i.r. spectra. Although one might expect the desired product, 1,1,1-trimethyl-disiloxane to disproportionate easily this is obviously not the case since no disiloxane was observed. The desired product must be decomposing by another route, probably induced by lithium silyl oxide. No hydrogen was detected. The overall reaction may be of the form:



This behaviour obviously constitutes a problem possibly related to the reactivity of lithium silyl oxide, that may be solved by the use of benzene.

#### Experimental

Lithium silyl oxide (0.3m mole) was prepared in an ampoule fitted with a greaseless tap. Trimethylsilyl chloride (0.3m mole) was distilled in and benzene (5mls) added. The reaction took place at room temperature for a few minutes. As before the volatile products consisted of silane (0.2m mole) and hexamethyl disiloxane. No hydrogen or disiloxane was observed.

#### Conclusion

The use of benzene as a solvent in the reaction of lithium silyl oxide and trimethylsilyl chloride does not alter the reaction course relative to that when diethyl ether is used as a solvent.

#### Experiment 4.39

##### The reaction of trimethylamine and lithium silyl selenide.

Trimethylamine (2m mole) was added to lithium silyl selenide (0.4m moles) in an n.m.r. tube using diethyl ether as a solvent. No insoluble material was formed at room temperature and no hydrogen or silane was detected. The  $^1\text{H}$ -n.m.r. spectrum showed trimethylamine and lithium silyl selenide with their  $^1\text{H}$ -n.m.r. parameters normal except for one important respect; the  $^{77}\text{Se}$  satellites of lithium silyl selenide were apparent at room temperature and did not sharpen up on

cooling. The  $^{77}\text{Se}$  chemical shift was also slightly (but significantly) different,  $-751 \pm 1$  p.p.m. as compared to the normal value of  $-736 \pm 1$  p.p.m.

#### Conclusion

Lithium silyl selenide does not decompose in the presence of trimethylamine but may well form a complex with it, which causes the rate of Se-Si bond cleavage in the anion to decrease. It should be noted that addition of a small amount (0.05m mole) of trimethylamine to lithium silyl selenide (0.4m mole) does not cause the  $^{77}\text{Se}$  satellites to be observed at room temperature. This dispels any possibility that trimethylamine is reacting with a small amount of impurity catalysing the Si-Se bond cleavage.

#### Experiment 4.40

##### The reaction of lithium silyl selenide, disilyl selenide and trimethylamine.

This reaction was carried out with trimethylamine (0.2m mole), disilyl selenide (0.2m mole) and lithium silyl selenide (0.2m mole) in an n.m.r. tube with diethyl ether as a solvent. On warming to room temperature no insoluble material formed. The temperature dependent  $^1\text{H}$ -n.m.r. spectrum obtained was very similar to that obtained for A MIXTURE OF disilyl selenide and lithium silyl selenide. i.e. a time averaged silyl resonance was observed from  $+28^\circ$  to  $-80^\circ$ .

#### Conclusion

Since no insoluble material was observed this implies that trimethylamine interacts preferentially with the anion. (a separate experiment showed that disilyl selenide and trimethylamine in diethyl ether produced a white insoluble material considered to be an adduct). This does not appear to reduce significantly the rate of Si-Se bond cleavage.

Experiment 4.41The reaction of lithium silyl oxide,  
disilyl selenide and trimethylamine.

This reaction was carried out with trimethylamine (0.5m mole), lithium silyl oxide (0.3m mole) and disilyl selenide (0.2m mole). The lithium silyl oxide was allowed to mix with the trimethylamine before the disilyl selenide was added. As before the system was studied in an n.m.r. tube with diethyl ether as a solvent. On warming the mixture to room temperature no solid was formed. The  $^1\text{H}$ -n.m.r. spectrum was identical to that obtained previously for lithium silyl oxide and disilyl selenide in the absence of trimethylamine. (see experiment 4.32).

Conclusion

Trimethylamine does not significantly change the kinetics or thermodynamics of the system, lithium silyl oxide/disilyl selenide/lithium silyl selenide/disiloxane. It should be noted that this system is probably quite sensitive to changes in kinetics or thermodynamics.

Experiment 4.42The reaction of trimethylsilyl chloride,  
lithium silyl selenide and trimethylamine

Lithium silyl selenide (0.4m mole) was prepared in an ampoule fitted with a greaseless tap. Trimethylamine (1 m mole) was added with diethyl ether as solvent and the reactants allowed to warm to room temperature. A clear solution resulted. Trimethylsilyl chloride (0.4m mole) was distilled into the ampoule and the reaction allowed to proceed at room temperature for a few minutes. A white solid, presumed to be lithium chloride, was formed immediately. The volatile products were then investigated.



Products were identified by their i.r. spectra. They consisted of diethyl ether and trimethylamine which passed  $-64^{\circ}$  and a volatile solid which stopped easily at  $-64^{\circ}$ . The i.r. spectrum of the vapour above this solid was consistent with its formulation as an adduct of trimethylsilyl silyl selenide and trimethylamine. It was not possible to isolate the components of the adduct by trap to trap distillation. Boron trifluoride (0.4m mole) was carefully added to the adduct so that reaction took place mainly in the vapour phase and a white film, considered to be a trimethylamine/boron trifluoride adduct was formed rapidly. The volatile products consisted of trimethylsilyl silyl selenide and a small amount of boron trifluoride. No decomposition products such as silyl fluoride were observed. The boron trifluoride could not be separated from the trimethylsilyl silyl selenide by trap to trap distillation. However, addition of excess diethyl ether formed a strong adduct with the boron trifluoride which took the form of a viscous liquid, and the trimethylsilyl silyl selenide could be easily separated from the diethyl ether by fractionation at  $-64^{\circ}$ . The yield of trimethylsilyl silyl selenide was 0.2m mole (50% based on  $\text{SiH}_3$ ). This is a bit low for this reaction but it is very possible that some of the product was "lost" when transferring it from one part of the line to another especially when it was in the form of an adduct.

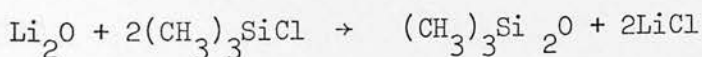
### Conclusion

The reaction of trimethylsilyl chloride and lithium silyl selenide is not detrimentally affected by the presence of trimethylamine. Removal of all of the trimethylamine does present a problem but in this particular case it can be done.



Experiment 4.43The reaction of trimethylsilyl chloride and  
lithium silyl oxide in the absence of solvent.

Lithium silyl oxide (0.2m moles) was prepared as usual in an ampoule fitted with a greaseless tap. It was pumped on for several hours to remove as much diethyl ether as possible. Most of the solid was located in the bottom half of the ampoule. Trimethylsilyl chloride (0.4m moles) was condensed into the top part of the ampoule and allowed to warm to room temperature for a few minutes. All of the reaction products were distilled into an n.m.r. tube. No hydrogen was formed. This procedure was used rather than attempting to fractionate the products on the vacuum line since 1,1,1-trimethyl disiloxane is known to disproportionate to hexamethyl disiloxane and disiloxane easily. It was felt particularly important to establish whether hexamethyl disiloxane was present or not since the possibility of lithium oxide as an impurity in lithium silyl oxide had not been discounted and hexamethyl disiloxane could be formed by the reaction.

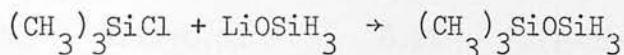


Using benzene as a solvent the  $^1\text{H}$ -n.m.r. spectrum was recorded. This showed the excess trimethylsilyl chloride at  $9.75 \pm 0.01$  p.p.m. (literature  $9.75 \pm 0.01$  p.p.m.), a small amount of diethyl ether and two peaks in the ratio of 1:3 at  $5.29 \pm 0.01$  p.p.m. and  $9.84 \pm 0.01$  p.p.m. respectively, assigned to 1,1,1-trimethyl disiloxane. The literature values are 5.39 and 9.92 p.p.m.<sup>20</sup>, measured in cyclohexane. Chemical shifts are often slightly different in cyclohexane and benzene. No disiloxane, silane or hexamethyl disiloxane was observed. The ratio of the methyl resonances of trimethylsilyl chloride and 1,1,1-trimethyl disiloxane was approximately 7 to 5 giving a yield of the desired

product of at least 70%. The experiment was repeated and the i.r. spectrum of the product confirmed that no hexamethyl disiloxane or disiloxane was produced ~~AND~~ that 1,1,1-trimethyl disiloxane WAS formed.<sup>20</sup>

### Conclusion

The reaction of trimethylsilyl chloride and lithium silyl oxide in the absence of solvent produces 1,1,1-trimethyl disiloxane in high yield. No hexamethyl disiloxane was produced and so lithium oxide was considered to be absent from the lithium silyl oxide. The overall reaction was considered to be:



The diethyl ether present in the sample was almost certainly complexed with the silyl anion and released when it reacted.

### Experiment 4.44

The reaction of lithium disilyl phosphide  
and hydrogen sulphide in the absence of a  
solvent.

### Introduction

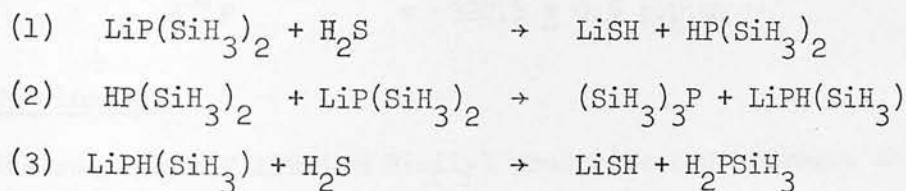
The reaction of lithium disilyl phosphide (0.3m mole) and an excess of hydrogen sulphide (1m mole) was carried out in an ~~AMPOULE~~ fitted with a greaseless tap. Diethyl ether was used as a solvent and the reaction allowed to proceed at  $-96^\circ$  for ten minutes. The excess of hydrogen sulphide was removed by fractionating the products from  $-96^\circ$ , through  $-120^\circ$  to  $-196^\circ$ . Hydrogen sulphide passed  $-120^\circ$  while all other products stopped at  $-120^\circ$  or  $-96^\circ$ . The procedure was adopted since hydrogen sulphide rapidly forms disilyl sulphide with silyl phosphines at room temperature. All the material that

stopped at  $-120^{\circ}$  and  $-96^{\circ}$  was distilled into an n.m.r. tube. The  $^1\text{H}$ -n.m.r. spectrum showed trisilylphosphine, disilylphosphine and monosilylphosphine to be present in the approximate ratio of 1:3:1.

The data obtained is shown below

<u>Compound</u>	<u>Chemical Shift (p.p.m.)</u>			<u>Couplings</u>	
	<u>Observed</u>	<u>Literature</u>		<u>Observed</u>	<u>Literature</u>
$(\text{SiH}_3)_3\text{P}$	$6.12 \pm 0.01$	6.09	$^2\text{J}(\text{P-Si-H})$	$16.7 \pm 0.4$	$16.9^{21}$
$(\text{SiH}_3)_2\text{PH}$	$6.06 \pm 0.01$	6.30	$^2\text{J}(\text{P-Si-H})$	$17.2 \pm 0.4$	$17.5 \pm 0.2^{22}$
			$^3\text{J}(\text{H-P-Si-H})$	$5.1 \pm 0.4$	$5.1 \pm 0.1$
$(\text{SiH}_3)\text{PH}_2$	$6.12 \pm 0.01$	6.27	$^2\text{J}(\text{P-Si-H})$	$16.2 \pm 0.4$	$16.2 \pm 0.2^{23}$
			$^3\text{J}(\text{H-P-Si-H})$	$5.1 \pm 0.4$	$5.1 \pm 0.1$

These products were considered to arise as follows:



It is reaction (2) that is of critical importance. Indeed, this is the reaction that one would wish to stop. For this reason the reaction was carried out in the absence of any solvent

### Experimental

Lithium disilyl phosphide (0.3m moles) was prepared as before and pumped on for several hours to remove any solvent. Most of the solid was located in the bottom of the ampoule. Hydrogen sulphide (1 m mole) was condensed into the ampoule and the reaction allowed to take place at  $-96^{\circ}$  for ten minutes. The excess of hydrogen sulphide was removed as before, using a  $-120^{\circ}$  slush bath. The volatile products consisted of disilylphosphine and a trace of diethyl ether, identified by their

i.r. spectra. The latter was removed by fractionation at  $-78^{\circ}$ . The  $^1\text{H}$ -n.m.r. spectrum of the sample confirmed the presence of disilylphosphine and also showed small quantities of disilyl sulphide and monosilylphosphine (approximately 5% of total Si-H present, based on signal intensities). The latter products probably arose by the exchange reaction of hydrogen sulphide and disilylphosphine.

Some n.m.r. parameters of disilylphosphine are included since they have not been previously reported.

Relative signs of coupling constants:

$^3J(\text{H-Si-P-H})$	positive
$^2J(\text{P-Si-H})$	positive
$^1J(\text{P-H})$	positive
$\delta^{31}\text{P}$	$= -322.5 \pm 0.5 \text{ p.p.m.}$

Conclusion

The reaction of lithium disilyl phosphide and hydrogen sulphide in the absence of solvent produces disilylphosphine as the main silyl product. Decomposition of the product to monosilyl phosphine and trisilylphosphine has almost been eliminated.

DISCUSSION

The preceding experiments have shown that:

- (a) The use of benzene as a solvent in the reactions of silyl anions does not inhibit side reactions.
- (b) Although there may be an interaction between trimethylamine and silyl anions it does not appear to solve the problem of side reactions.
- (c) The absence of solvent in the reactions of the silyl anions does appear to reduce side reactions to a considerable extent.

It is not too surprising that trimethylamine does not reduce side reactions. Even if it did it would almost certainly introduce problems of its own. For instance, in the experiment 4.42 purification difficulties were encountered which arose from the interaction of trimethylamine and silyl compounds. The use of benzene as a solvent would appear to be an unfruitful approach to the problem but in many ways it is equivalent to the solid/gas reactions. Since these reactions were considered to be successful in the two experiments attempted it suggests that a modification of the asolvic approach

would be more successful. For instance, a larger surface area of solid could be used in reactions. It should be noted that disilylphosphine and 1,1,1-trimethyl disiloxane are generally considered to be sensitive molecules in that both readily decompose or disproportionate. The fact that both of these molecules can be prepared by using silyl anions in the absence of a solvent, but not in the presence of solvent, must mean that the reactivity of the anions has been modified.



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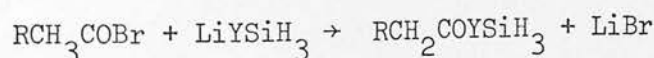
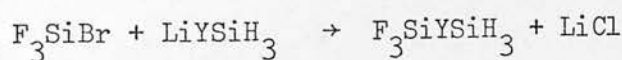
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### SUGGESTIONS FOR FURTHER WORK

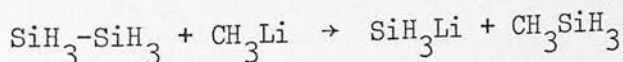
Ammonium silyl telluride has most probably the same potential as the other ammonium salts that have been previously prepared. For instance, the synthesis of acetyl silyl telluride would be of interest. Extension of the method of preparation of these ammonium salts seems unlikely e.g.



The lithium silyl anions of Group V and VI may well be useful synthetic reagents, especially in view of the experiments carried out in chapter 4(c) where it was shown that disilyl phosphine and 1,1,1-trimethyl disiloxane could be prepared in high yield. Under these conditions many reactions of interest could be carried out with a good chance of success e.g.



Extension of the method of preparation of these anions seems possible especially in view of some of the reactions of silyl anions with acetyl derivatives. Some experiments have already been carried out that suggest that the following reactions take place



The latter reaction is particularly interesting.

## APPENDIX 1

### THE SILICON-SULPHUR BOND IN LITHIUM SILYL SULPHIDE

## INTRODUCTION

Many attempts using various techniques have been made to demonstrate that  $p \rightarrow d$ ,  $\Pi$  bonding occurs to a significant extent in silicon compounds.<sup>1,2,3</sup> Almost invariably these attempts have led to conclusions that are only tentative. Lithium silyl sulphide is a particularly suitable compound for investigating this problem in that the ion,  $^-SSiH_3$ , is a small species of high symmetry with a considerable amount of negative charge associated with the sulphur atom. Although the lithium-sulphur bond is probably not totally ionic it is reasonable to assume that the  $SiH_3S^0$  species behaves as an isolated unit.

The simplest way of estimating the effect of the negative charge on sulphur, on the silicon-sulphur bond in lithium silyl sulphide, is to compare the silicon-sulphur stretching frequencies and force constants of related molecules. Disilyl sulphide was chosen as a suitable molecule for comparison. It should however be noted that a force constant for a particular vibration is only a measure of the curvature at the bottom of the potential well and is not directly related to bond strengths. Throughout this work it is assumed that a larger force constant for a vibration implies an increased bond strength. This seems to be intuitively correct for most cases. In this work it is also assumed that the silyl-thio anion can be treated as a diatomic. This assumption can be partially justified by showing that using an accurately determined value of the force constant for  $\nu_3$  in disilyl sulphide and treating it as a triatomic does not lead to any large error in the predicted value of the frequency of  $\nu_3$ . It should also be stressed that only "simple-minded" arguments are used in this work and it is not intended that they prove the existence of  $p \rightarrow d$ ,  $\Pi$  bonding but only show that it is a reasonable interpretation.

CALCULATIONS(a) The effect of treating disilyl sulphide as a triatomic

Assume that disilyl sulphide can be treated as a triatomic molecule made up of two masses of 31 and one of 32, therefore the equation below is valid.<sup>4</sup>

$$kv_3^2 = (f_r - f_{rr}) \left( \frac{1}{31} + \frac{2}{32} \sin^2 \theta \right) \quad (1)$$

where  $\theta$  = half of the apex angle in disilyl sulphide

$k$  = conversion constant

$v_3$  = the frequency of the asymmetric stretch in disilyl sulphide

$f_r$  = force constant for  $v_3$

$f_{rr}$  = interaction constant for  $v_3$

Values of  $\theta, k, f_r, f_{rr}$  and  $k$  have been derived.<sup>5</sup> Inserting these values ( $\theta = 48.7^\circ$ ,  $k = 0.59 \times 10^{-6}$ ,  $f_r = 2.35 \text{ m.dyne } \text{\AA}^{-1}$  and  $f_{rr} = 0.01$ ) into equation (1) gives a value of  $v_3$  of  $517.5 \text{ cm}^{-1}$ . The observed frequency of  $v_3$  is  $517 \text{ cm}^{-1}$ . Thus the assumptions made appear to be valid.

(b) The force constant for the silicon-sulphur stretch ( $v_2$ ) in lithium silyl sulphide.

Assuming that the silyl-thio anion can be treated as a diatomic the force constant for  $v(\text{Si-S})$  can be calculated as follows:-

For a diatomic made up of two masses of 31 and 32 then the equation below is valid.<sup>4</sup>

$$kv^2 = f_r \left( \frac{1}{31} + \frac{1}{32} \right) \quad (2)$$

where  $k$  = conversion factor =  $0.59 \times 10^{-6}$

$v$  = frequency of the silicon-sulphur stretch

$f_r$  = force constant for  $v_2$

Inserting the appropriate values of  $v_2$  observed for the silyl anion gives

the following values of  $f_r$ .

$$1. \quad \nu = 565 \pm 5 \text{ cm}^{-1} \text{ (i.e. for Raman (solid))} \quad f_r = 2.76 \pm 0.05 \text{ m.dyne } \text{\AA}^{-1}$$

$$2. \quad \nu = 565 \pm 5 \text{ cm}^{-1} \text{ (i.e. for Raman as a solution in diethyl ether)}$$

$$f_r = 2.97 \pm 0.05 \text{ m.dyne } \text{\AA}^{-1}$$

$$3. \quad \nu = 530 \pm 5 \text{ cm}^{-1} \text{ (i.e. for solid i.r.)} \quad f_r = 2.61 \pm 0.05 \text{ m.dyne } \text{\AA}^{-1}$$

It should be noted that in all cases the value of  $f_r$  is appreciably higher than for the corresponding vibration in disilyl sulphide. In fact for  $f_r = 2.30 \text{ m.dyne } \text{\AA}^{-1}$  a value of  $\nu = 498 \text{ cm}^{-1}$  would be predicted.



## DISCUSSION

The preceding calculations have shown that the force constant for the silicon-sulphur stretch in the silyl-thio anion is appreciably greater than in the corresponding vibration in disilyl sulphide. This is interpreted as showing that the silicon-sulphur bond of the former is stronger. The aim of this discussion is to show that this could arise from  $p \rightarrow d$ ,  $\Pi$  bonding from sulphur to silicon.

It is obvious that any donation of negative charge to silicon from sulphur in the anion would lead to more negative charge on silicon relative to disilyl sulphide. It is difficult to show this but assuming that, at least in part, the  $^{29}\text{Si}$  chemical shifts of these molecules are a reflection of the amount of negative charge on silicon then their values are important; in disilyl sulphide  $\delta^{29}\text{Si}$  is  $-47 \pm 1$  p.p.m.<sup>6</sup> and lithium silyl sulphide has  $\delta^{29}\text{Si}$  equal to  $-58 \pm 1$  p.p.m. It is pertinent to note that the  $^{29}\text{Si}$  chemical shift range is normally considered to be small.<sup>7</sup> These values are consistent with more negative charge on the Si atom of the anion relative to disilyl sulphide.

There are two distinct ways in which a negative charge on sulphur can lead to a stronger silicon-sulphur bond. One is to postulate a sigma ( $\sigma$ ) effect and the other a  $\Pi$  effect. The former implies that  $\text{S}^-$  forms a stronger  $\sigma$  bond to silicon than a neutral sulphur atom. The latter implies a  $p \rightarrow d$ ,  $\Pi$  interaction. The choice between  $\sigma$  and  $\Pi$  effects is one that occurs frequently in qualitative arguments and indeed it can be an insurmountable problem. In this case the following argument is an attempt to overcome this difficulty.

The strength of a silicon-sulphur  $\sigma$  bond depends, in part, on the

electronegativity difference between silicon and sulphur. The sulphur atom is the more electronegative.<sup>8</sup> If one puts a negative charge on sulphur it seems reasonable to propose that it will become less electronegative. Thus the strength of the silicon-sulphur  $\sigma$  bond must decrease or at least not increase. On the other hand a  $\Pi$  effect giving rise to multiple bonding could increase the silicon-sulphur bond strength. It is therefore contended that the increase in bond strength of the silicon-sulphur bond in the silyl anion must be caused by  $\Pi$  bonding. An interaction between the sulphur orbitals and the  $\text{SiH}_3$  antibonding orbitals is possible but seems unlikely in view of the fact that the frequencies of  $\nu$  Si-H for the anion are normal. This leaves  $p \rightarrow d$ ,  $\Pi$  bonding as the most plausible alternative. The argument described above can be justified to some extent. The frequencies for the silicon-sulphur stretch in ammonium silyl sulphide are  $550 \text{ cm}^{-1}$  (from i.r.) and  $551 \text{ cm}^{-1}$  (from Raman)<sup>9</sup>. These are also appreciably higher than in disilyl sulphide and dispel any doubts about the influence of the cation. In the analogous methyl compounds no increase in  $\nu(\text{C-S})$  is found. For example in dimethyl sulphide  $\nu_{\text{asym}} \text{C}_2\text{S}$  is at  $694 \text{ cm}^{-1}$  and  $\nu_{\text{sym}} \text{C}_2\text{S}$  is at  $742 \text{ cm}^{-1}$ ,<sup>10</sup> while in tetramethyl phosphonium methyl sulphide  $\nu \text{C-S}$  is at  $705 \text{ cm}^{-1}$ .<sup>11</sup> These values represent the acid test for all of the arguments used here since  $p \rightarrow d$ ,  $\Pi$  bonding for carbon compound is generally considered to be insignificant.

## CONCLUSION

It has been shown that the force constant for  $\nu \text{Si-S}$  in lithium silyl sulphide is larger than the analogous vibration in disilyl sulphide. This has been attributed to a stronger Si-S bond in the anion. It has also been shown that the increase in bond strength is consistent with  $p \rightarrow d$ ,  $\Pi$  bonding in the anion.

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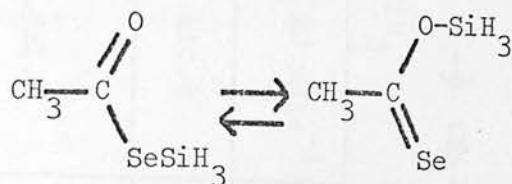
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## APPENDIX 2

### A LINE SHAPE ANALYSIS OF THE TEMPERATURE DEPENDENT $^1\text{H}$ -n.m.r. SPECTRUM OF ACETYL Silyl SELENIDE.

## INTRODUCTION

It has been shown<sup>1</sup> that acetyl silyl selenide exhibits a temperature dependent <sup>1</sup>H-n.m.r. spectrum corresponding to the process



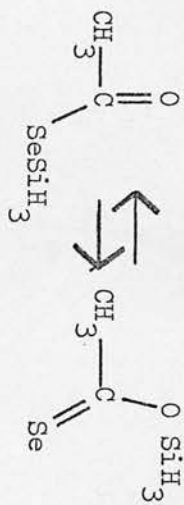
A relatively pure sample of acetyl silyl selenide (90%) was prepared by the method previously outlined (see Chapter 4). Using a computer program written by Nakagawa<sup>2</sup> and modified by Dr R.K. Harris a line shape analysis was carried out on the temperature dependent spectra obtained. The analysis was carried out for samples in three different solvents: tetramethyl silane, a 50-50 mixture of benzene and carbon tetrachloride and diethyl ether. A summary of the results obtained is shown in table A2.1



For the sake of clarity an outline of the method used in this calculation has been included. It should be stressed that this is not intended to be a rigorous treatment.

In a normal n.m.r. experiment the molecules under study are usually considered to be permanent in the sense that they are held together by chemical bonds which have a very long lifetime. These types of molecules give n.m.r. spectra that are not a function of temperature. If the nuclei in the molecule being studied are not fixed but are able to migrate from one site in the molecule to another then this may affect the observed n.m.r. spectrum. Obviously the rate of the chemical exchange will determine the effect on the n.m.r. signals observed. If the rate is slow then the n.m.r. signals observed will consist of a super-imposition of the spectra of the various species.

TABLE A2.1

Some activation parameters for the process



SOLVENT												
	$E_a$ kJ Mole <sup>-1</sup>	$\Delta H_{298}^*$ kJ Mole <sup>-1</sup>	$\Delta S_{298}^*$ E.U.	$\Delta G_{298}^*$ kJ Mole <sup>-1</sup>	$E_a$ kJ Mole <sup>-1</sup>	$\Delta H_{298}^*$ kJ Mole <sup>-1</sup>	$\Delta S_{298}^*$ E.U.	$\Delta G_{298}^*$ kJ Mole <sup>-1</sup>				
I.M.S.	47.8±0.8	45.4±0.8	-52.4±8.5	61.0±3.3	47.9±1	45.4±1	-42.6±9.9	58.0±4.0				
$\text{CCl}_4 + \text{C}_6\text{H}_6$	56.0±1.6	53.5±1.6	-14.0±13.9	57.7±5.8	56.9±1.4	54.4±1.4	-31.6±16.8	63.8±6.4				
$(\text{C}_2\text{H}_5)_2\text{O}$	66.1±5.0	63.6±5.0	+19.4±73	58±29	69.7±2.9	67.2±2.9	+41±67	56±23				



If the exchange is very fast only one line will be observed corresponding to the mean position of the chemical shifts of the exchanging nuclei. Intermediate exchange rates will give spectra with broadened lines from which information concerning the rate can be determined.<sup>3</sup> In favourable cases all these regions of exchange can be observed by varying the temperature at which the spectra are run. (see figure A2.1)

Extensive theoretical work had been done on the effect of chemical exchange on the shapes of n.m.r. signals. Indeed the pioneers of nuclear magnetic resonance were mainly concerned with dynamic processes and line shapes. (The first observation of chemical shifts and coupling constants were entirely unexpected). In this work use was made of a computer program designed to study such systems available on file in the computer library.

The data required for the program to function consists of the frequency difference between the discrete n.m.r. signals, the natural line width and the population of the exchange sites. Given this information the program will print out a series of calculated n.m.r. spectra for various lifetimes of the exchange sites. In the example shown these were in the ranges

0.0001 seconds to 0.0009 seconds in steps of 0.0001 seconds

0.001        "        " 0.009        "        "        "        " 0.001        "

0.01        "        " 0.09        "        "        "        " 0.01        "

0.1        "        " 0.9        "        "        "        " 0.1        "

The values of the populations of the exchange sites can be calculated from the equilibrium constant for the reaction, using the relation.

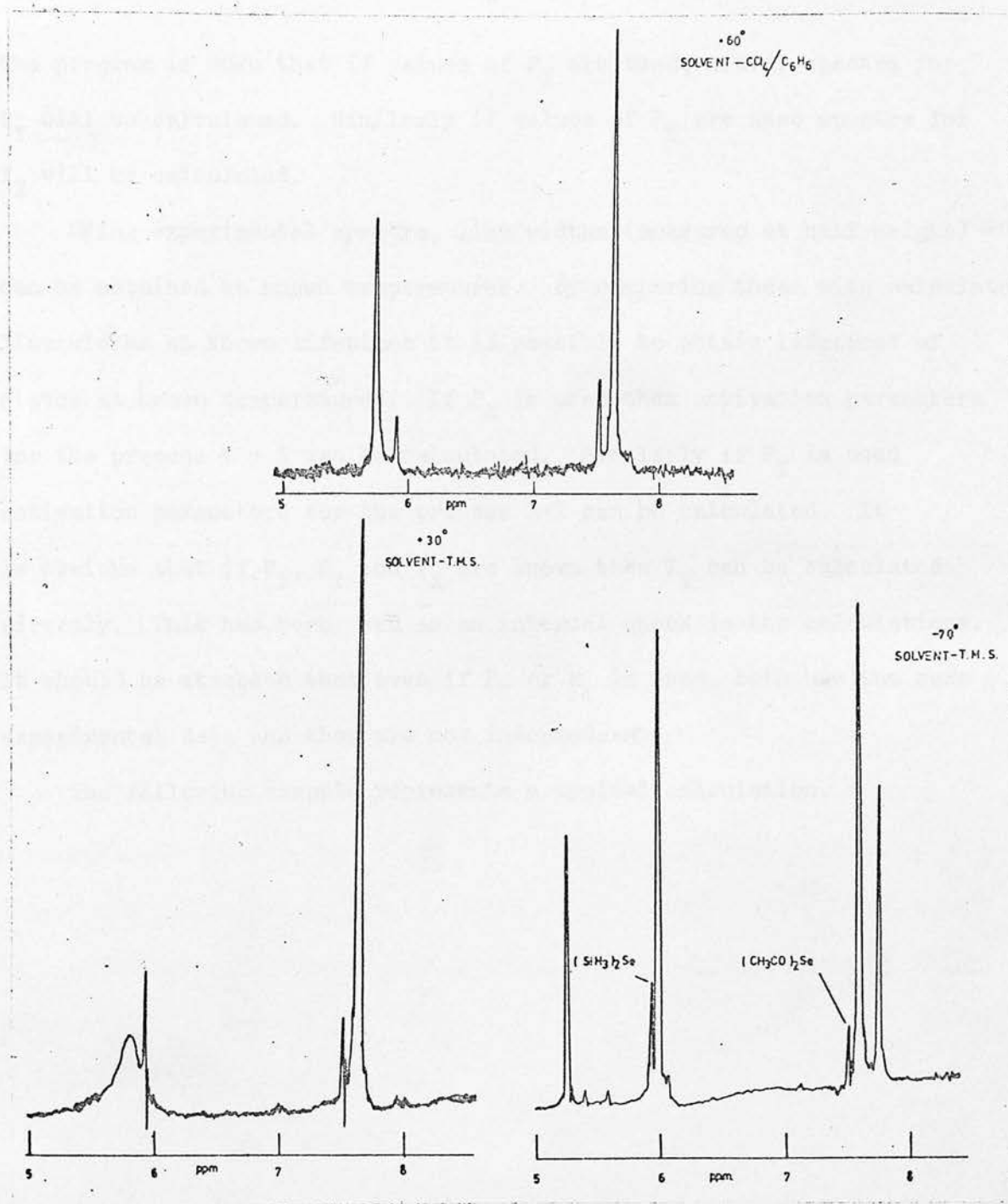
$$\frac{P_X}{P_Y} = K,$$

where  $P_X$  is the population of site X

$P_Y$  is the population of site Y

K is the equilibrium constant.

FIGURE A2.1



In general for a two side exchange between sites X and Y,

$$P_X T_Y = P_Y T_X \quad \text{where } T_Y \text{ is the lifetime of site Y}$$

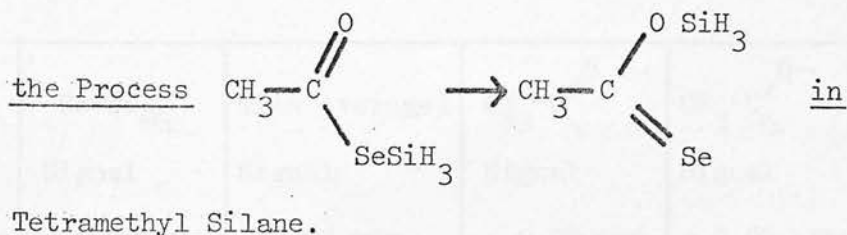
$$T_X \text{ is the lifetime of site X}$$

The program is such that if values of  $P_X$  are used, n.m.r. spectra for  $T_Y$  will be calculated. Similarly if values of  $P_Y$  are used spectra for  $T_X$  will be calculated.

Using experimental spectra, line widths (measured at half height) can be obtained at known temperatures. By comparing these with calculated line widths at known lifetimes it is possible to obtain lifetimes of states at known temperatures. If  $P_X$  is used then activation parameters for the process  $Y \rightarrow X$  can be calculated. Similarly if  $P_Y$  is used activation parameters for the process  $X \rightarrow Y$  can be calculated. It is obvious that if  $P_X$ ,  $P_Y$  and  $T_X$  are known then  $T_Y$  can be calculated directly. This has been used as an internal check in the calculations. It should be stressed that even if  $P_X$  or  $P_Y$  is used, both use the same experimental data and they are not independent.

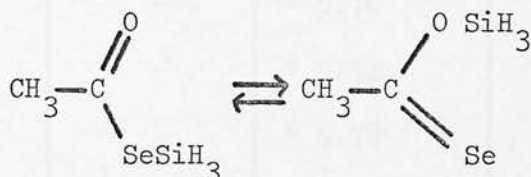
The following example represents a typical calculation.

The Calculation of the Activation Parameters for



For the purposes of this calculation the signals assigned to the time-averaged  $\text{SiH}_3$  resonances were used in the region of fast exchange, and the  $\text{SiH}_3\text{-Se}$  resonance in the region of medium and slow exchange.

(a) Calculation of the equilibrium constant K for the reaction



In the region of fast exchange, the time-averaged signals represent the weighted means of the "frozen out" signals. This affords a method of calculating the equilibrium constant. This assumes that the equilibrium constant does not vary with temperature. Since the time averaged n.m.r. signals are a sensitive reflection of the equilibrium constant and since their chemical shifts do not vary from + 30 to + 76 it is reasonable to suggest that it does not vary within the temperature range studied, (see table A.2.2).

From the  $\text{SiH}_3$  resonances:-

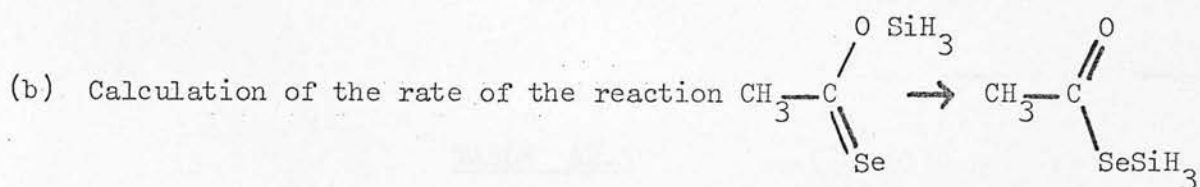
$$\begin{aligned} \text{Ratio of } \text{CH}_3-\text{C} \begin{array}{l} \text{O-SiH}_3 \\ \parallel \\ \text{Se} \end{array} \text{ to } \text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{SeSiH}_3 \end{array} &= \frac{19 \pm 1 \text{ Hz}}{75 \pm 1 \text{ Hz}} \\ &= \underline{0.26 \pm 0.01} \\ &= K \\ &= 1:4 \end{aligned}$$

TABLE A2.2

## Variation of chemical shifts with temperature

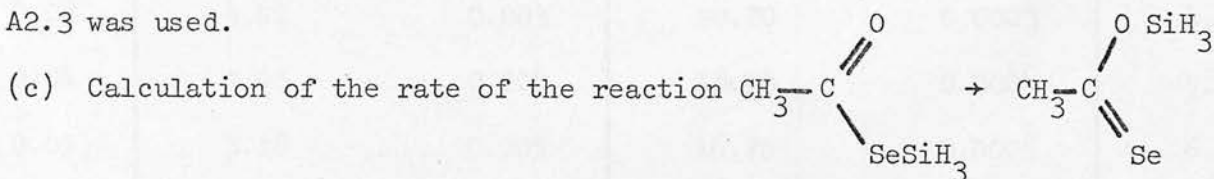
Temperature °C	$\text{-O-SiH}_3$ Signal $\pm 0.02$ ppm	$\text{-Se-SiH}_3$ Signal $\pm 0.02$ ppm	Time averaged Signal $\pm 0.02$ ppm	$\text{CH}_3\text{-C}(=\text{O})$ Signal $\pm 0.02$ ppm	$\text{CH}_3\text{-C}(=\text{O})\text{-O-}$ Signal $\pm 0.02$ ppm	Time averaged Signal $\pm 0.02$ ppm
+67.5	-	-	5.78	-	-	7.69
60	-	-	5.78	-	-	7.69
55	-	-	5.78	-	-	7.69
50	-	-	5.78	-	-	7.69
45	-	-	* 5.78	-	-	7.69
40	-	-	* 5.78	-	-	7.69
37.5	-	-	* 5.78	-	-	7.69
32.5	-	-	* 5.78	-	-	7.69
29.5	-	-	* 5.78	-	-	7.69
20	-	* 5.87	-	-	-	* 7.69
14	n.o.	* 5.93	-	-	-	* 7.69
10	n.o.	* 5.94	-	-	-	* 7.69
5	n.o.	* 5.96	-	-	-	* 7.69
0	n.o.	* 5.97	-	-	-	* 7.69
-5	5.31	5.98	-	* 7.65	* 7.75	-
-32.5	5.31	5.98	-	7.65	7.75	

\* Estimates of broad signals-error  $\pm 0.1$  p.p.m.Solvent -  $\text{CCl}_4/\text{C}_6\text{H}_6$ .



at various temperatures.

This calculation was carried out using the computer programme as outlined in the introduction. Table A2.3 shows the lifetimes and line widths derived from the computer program. Table A2.4 shows calculated lifetimes at known temperatures and hence the rate. It should be noted that linear interpolation between the calculated lifetimes on table A2.3 was used.

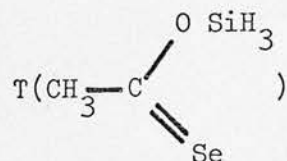


This calculation was exactly the same as the one above except that a different population of the exchange site was used (see introduction). In addition a crosscheck could be used for the lifetimes calculated, by using the relation

$$T(\text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{SeSiH}_3 \end{array}) = T(\text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{Se} \end{array} \begin{array}{l} \text{O} \\ \text{SiH}_3 \end{array}) \times \frac{1}{K}$$

where  $T(\text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{SeSiH}_3 \end{array})$  is the lifetime of  $\text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{SeSiH}_3 \end{array}$  and

similarly for



Tables A2.5 and A2.6 are completely analogous to tables A2.3 and A2.4 respectively.

(d) From the corresponding values of the rates of reaction and temperature an Arrhenius plot could be made as is shown in figure A2.2



TABLE A2.3

T(S)	L.W. (Hz)	T(S)	L.W. (Hz)	T(S)	L.W. (Hz)
0.01	9.90	0.001	10.50	0.0001	2.56
0.02	6.01	0.002	17.60	0.0002	3.54
0.03	4.42	0.003	20.70	0.0003	4.42
0.04	3.98	0.004	18.90	0.0004	5.30
0.05	3.18	0.005	16.75	0.0005	6.80
0.06	2.83	0.006	14.65	0.0006	7.06
0.07	2.65	0.007	13.08	0.0007	8.04
0.08	2.56	0.008	12.00	0.0008	8.84
0.09	2.38	0.009	11.30	0.0009	9.71

T = Lifetime of exchange site

L.W. = Line Width

TABLE A2.4

Observed L.W. (Hz)	T(S)	Rate ( $\frac{1}{T}$ ) $\times 10^{-3}$	$\text{Log}_{10}$ Rate	$\frac{1}{T} \times 10^3 \text{ } ^\circ\text{K}^{-1}$
7.5	0.00064	1.564	3.194	3.14
10.0	0.00094	1.065	3.027	3.19
12.5	0.0013	0.769	2.886	3.25
16.0	0.0018	0.556	2.745	3.30
19.4	0.0024	0.417	2.620	3.36
19.5	0.0037	0.271	2.433	3.41
16.5	0.0051	0.196	2.292	3.47
14.5	0.0061	0.164	2.215	3.53
11.0	0.0092	0.109	2.037	3.60
7.5	0.016	0.0625	1.800	3.66
6.5	0.019	0.526	1.721	3.73
4.5	0.03	0.0334	1.524	3.83

TABLE A2.5

T(S)	L.W. (Hz)	T(S)	L.W.	T(S)	L.W.
0.1	4.77	0.01	19.60	0.001	3.97
0.2	3.18	0.02	16.05	0.002	6.54
-	-	0.03	12.00	0.003	8.83
-	-	0.04	9.35	0.004	11.30
-	-	0.05	7.85	0.005	13.40
-	-	0.06	7.05	0.006	15.00
-	-	0.07	6.09	0.007	16.85
-	-	0.08	5.56	0.008	18.25
-	-	0.09	5.12	0.009	19.60

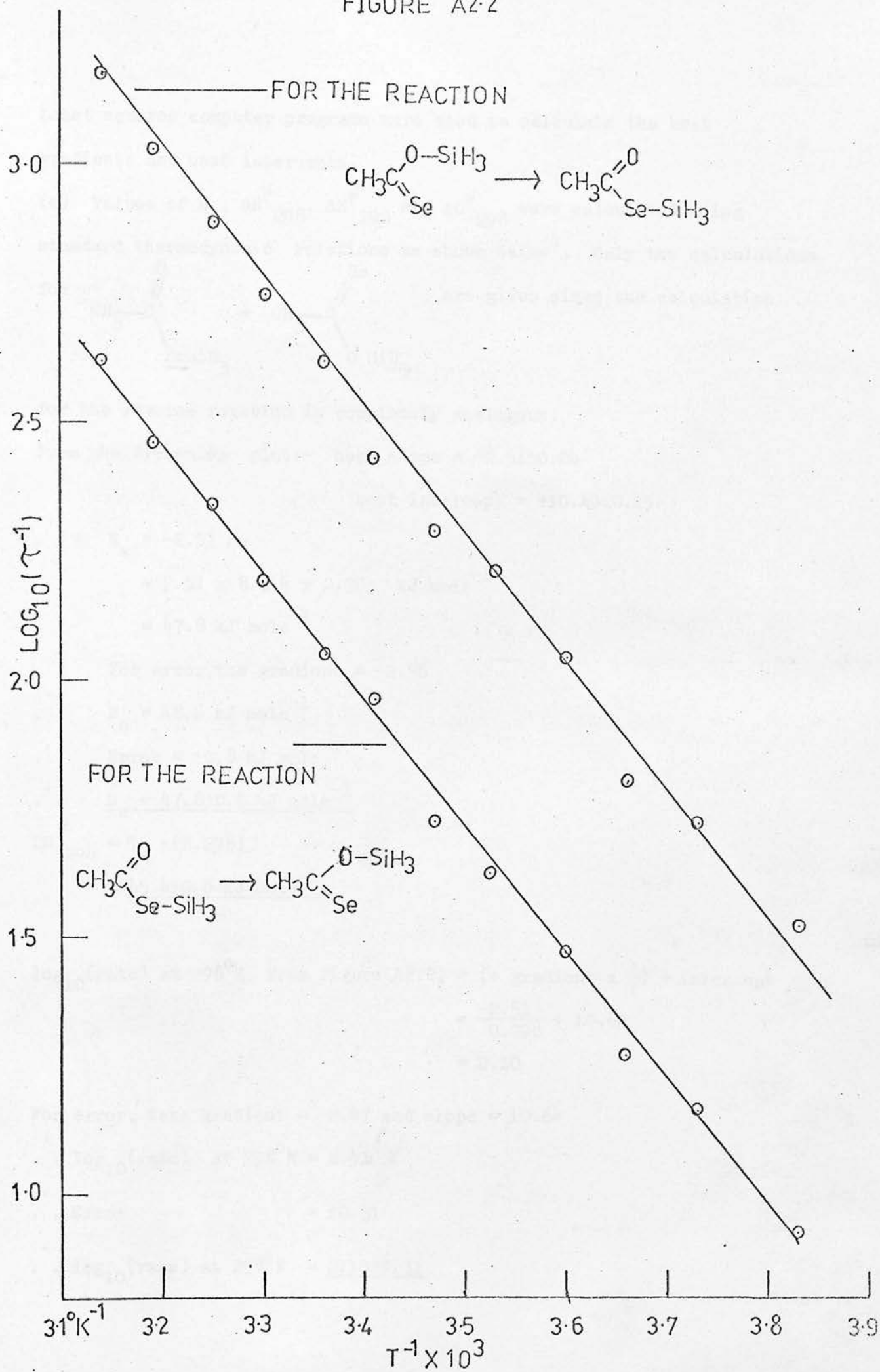
L.W. = Line Width

TABLE A2.6

Observed L.W.	$\tau$ (S)	Predicted $\tau$ (S)	Rate ( $1/\tau$ ) $\times 10^{-3}$	$\log_{10}(\text{rate})$	$\frac{1}{\tau} \times 10^3 \text{ } ^\circ\text{K}^{-1}$
7.5	0.0024	0.0024	0.417	2.620	3.14
10.0	0.0035	0.0035	0.286	2.456	3.19
12.5	0.0046	0.0048	0.218	2.339	3.25
16.0	0.0065	0.0067	0.158	2.188	3.30
19.4	0.0089	0.0089	0.112	2.050	3.36
19.5	0.011	0.014	0.0908	1.958	3.41
16.5	0.019	0.019	0.0526	1.721	3.47
14.5	0.024	0.023	0.0417	1.620	3.53
11.0	0.034	0.034	0.0294	1.468	3.60
7.5	0.054	0.059	0.0185	1.267	3.66
6.3	0.067	0.071	0.0149	1.173	3.73
4.5	0.12	0.011	0.00834	0.921	3.83

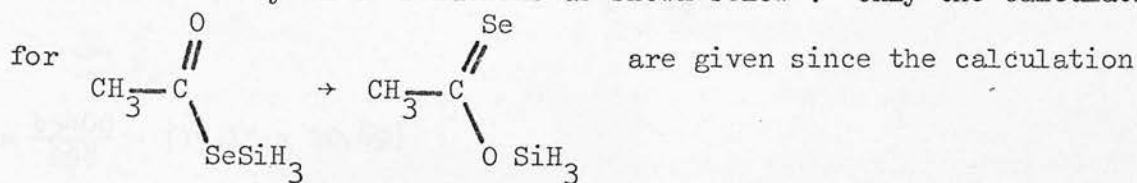
$\tau$  = Lifetime of exchange site

FIGURE A2.2



Least squares computer programs were used to calculate the best gradients and best intercepts.

(e) Values of  $E_a$ ,  $\Delta H^\ddagger_{298}$ ,  $\Delta S^\ddagger_{298}$  and  $\Delta G^\ddagger_{298}$  were calculated using standard thermodynamic relations as shown below<sup>4</sup>. Only the calculations



for the reverse reaction is completely analogous.

From the Arrhenius plot:- best slope =  $-2.51 \pm 0.04$

best intercept =  $+10.49 \pm 0.15$

$$\therefore E_a = -2.51 \text{ Re}$$

$$= 2.51 \times 8.314 \times 2.303 \text{ kJ mole}^{-1}$$

$$= 47.8 \text{ kJ mole}^{-1}$$

For error, the gradient =  $-2.56$

$$\therefore E_a = 48.6 \text{ kJ mole}^{-1}$$

$$\therefore \text{Error} = \pm 0.8 \text{ kJ mole}^{-1}$$

$$\therefore \underline{E_a = 47.8 \pm 0.8 \text{ kJ mole}^{-1}}$$

$$\Delta H^\ddagger_{298} = E_a - (R \cdot 298)$$

$$= \underline{45.4 \pm 0.8 \text{ kJ mole}^{-1}}$$

$$\begin{aligned} \log_{10}(\text{rate}) \text{ at } 298^\circ\text{K, from figure A2.2,} &= (+ \text{gradient} \times \frac{1}{T}) + \text{intercept} \\ &= \frac{-2.51}{0.298} + 10.49 \\ &= 2.10 \end{aligned}$$

For error, take gradient =  $-2.47$  and slope =  $10.64$

$$\therefore \log_{10}(\text{rate}) \text{ at } 298^\circ\text{K} = 2.41$$

$$\therefore \text{Error} = \pm 0.31$$

$$\therefore \log_{10}(\text{rate}) \text{ at } 298^\circ\text{K} = \underline{2.10 \pm 0.31}$$



$$DS_{298}^{\ddagger} = \frac{DH_{298}^{\ddagger}}{T} - R \ln \left[ \log_{10} \frac{kT}{h} - \log_{10} (\text{rate})_{298} \right]$$

where  $k$  = Boltzmann's constant

$h$  = Plank's constant

$T = 298$

$$= \frac{45400}{298} - (19.15 \times 10.69)$$

$$= -52.4 \text{ J mol}^{-1} \text{ } ^{\circ}\text{K}^{-1}$$

for error, take  $\Delta H^{\ddagger} = 44.6 \text{ kJ mol}^{-1}$

and  $\log_{10} (\text{rate})_{298} = 2.41$

$$\therefore \Delta S_{298}^{\ddagger} = -60.9$$

$$\therefore \text{Error} = \pm 8.5$$

$$\therefore \underline{DS_{298}^{\ddagger} = -52.4 \pm 8.5 \text{ J mol}^{-1} \text{ } ^{\circ}\text{K}^{-1}}$$

$$\Delta G_{298}^{\ddagger} = \Delta H_{298}^{\ddagger} - (T \Delta S_{298}^{\ddagger})$$

$$= 45400 - (298 \times 52.4)$$

$$= 61.0 \text{ kJ mole}^{-1}$$

For error, take  $\Delta H_{298}^{\ddagger} = 44.6 \text{ kJ mole}^{-1}$

and  $\Delta S_{298}^{\ddagger} = -43.9$

$$\therefore DG_{298}^{\ddagger} = 57.7 \text{ kJ mole}^{-1}$$

$$\therefore \text{Error} = 3.3 \text{ kJ mole}^{-1}$$

$$\therefore \underline{\Delta G_{298}^{\ddagger} = 61.0 \pm 3.3 \text{ kJ mole}^{-1}}$$

A note on the Calculation using Diethyl Ether as a Solvent.

As can be seen from the above calculation, errors in  $\Delta S_{298}^\ddagger$  are particularly bad. This is a regrettable but unavoidable characteristic of the calculation. In the case with diethyl ether as solvent the errors in  $\Delta S_{298}^\ddagger$  are so large that the results are not very meaningful: this arose because the temperature range over which the calculation was done had to be fairly small (248-273°K). The signal assigned to  $\text{SiH}_3\text{-O-}$  had to be used since other resonances were too close to the ether resonances to be of any value.

Calculation of some overall thermodynamic data.

As has been shown it was possible to obtain data for the activation process in the reaction, it was also possible to obtain some overall thermodynamic data.

Since the system is at equilibrium (all processes were reversible) the overall free energy change  $\Delta G$  must be zero. It was shown that the equilibrium constant for the reaction was not a function of temperature, since no change in the chemical shifts of the time-averaged signals could be detected as the temperature was varied (see table A2.2) using the equation

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

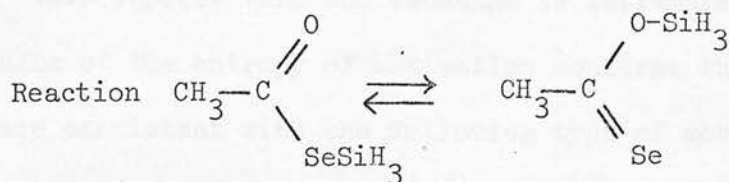
The value of  $\Delta H^\circ$  must be zero (or very small) and so, values of  $\Delta S^\circ$  can be calculated. Values of  $\Delta G^\circ$  can also be calculated using

$$\Delta G^\circ = -RT \ln K$$

The data obtained for the solvents used is shown in table A2.7

TABLE A2.7

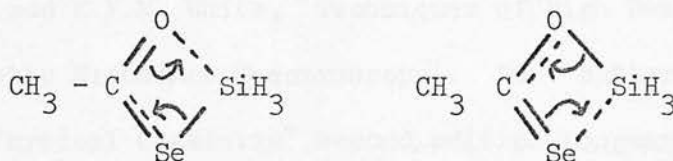
Overall Thermodynamic Data for the



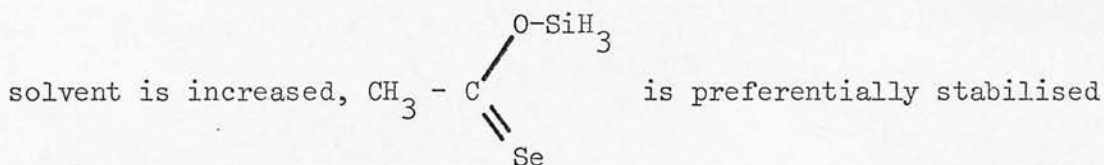
Solvent	$\Delta H^\circ$ kJ Mole <sup>-1</sup>	$\Delta S^\circ$ E.U.	$\Delta G^\circ$ kJ Mole <sup>-1</sup>	K
Tetramethyl Silane	~ 0	~ -2.1	3.3±0.1	0.26±0.01
Benzene + Carbon Tetra- chloride	~ 0	~ 1.9	3.0±0.1	0.30±0.01
Diethyl Ether	~ 0	~ 1.6	2.0±0.1	0.45±0.01

# DISCUSSION

It was shown that the rate of the reaction was independent of concentration. This implies that the exchange is intramolecular. The negative value of the entropy of activation confirms this conclusion. These results are consistent with the following type of mechanism.



It is surprising that  $\Delta H^\circ$  for the reaction is zero since a fine balance of bond energies is implied. Since  $\Delta H^\circ$  is zero, the value of the equilibrium constant is determined by  $\Delta S^\circ$ . This is demonstrated by the slight variation of  $K$  with solvent. As the polarity of the



to a small extent. This may be a reflection of the difference in the polarity of the two isomers.

It has also been observed that  $E_a$  and  $\Delta H^\ddagger_{298}$  increase with increasing polarity of solvent. This can be rationalised in terms of a decrease in the polarity of the molecule when it passes through the activated complex.

It is pertinent to point out that the  $^1\text{H}$ -n.m.r. spectrum of the analogous sulphur compound shows no apparent temperature dependence in the range  $-60^\circ\text{C}$  to  $+50^\circ\text{C}$  in T.M.S. This must mean that either  $K$  is very far from unity or that the exchange reaction is very fast. The former possibility seems the more likely.

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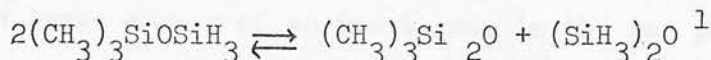
### APPENDIX 3

The exchange reaction of  $H_6$ -disilyl  
selenide and  $D_6$ -disilyl selenide.

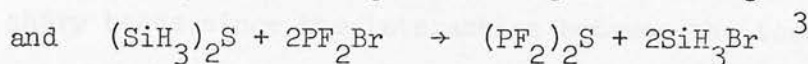


## INTRODUCTION

For some years it has been known that a silyl group attached to a group VI element is labile. For instance, 1,1,1-trimethylsilyl silyl ether disproportionates readily in the liquid phase



and group VI silyl derivatives will undergo exchange reactions e.g.



This behaviour has been the subject of some discussion in the preceding thesis, in the formation of silyl anions and in possible mode of decomposition of products involving silyl anions. The following experiments highlight the ease of cleavage of a Si-Se bond in disilyl selenide in the absence of any obvious catalyst or powerful thermodynamic pull on the reaction.

Matrix isolation techniques were used to study the exchange reaction of  $\text{H}_6$ -disilyl selenide and  $\text{D}_6$ -disilyl selenide by observing i.r. spectra at  $10^\circ\text{K}$ . This technique is a relatively new one and not generally used for this purpose. For these reasons a brief account of the technique is as follows:-

In a normal gas phase i.r. spectrum recorded at room temperature, the "natural line width" of bands is usually of the order of  $20\text{ cm}^{-1}$ . Part of this band width is caused by rotational transitions superimposed on vibrations. At room temperature many rotational quantum states are populated to a significant extent. As the sample is cooled the extent of population of rotational states decreases and so the "natural line

width" decreases. Unfortunately, if the sample is cooled too far it may form a liquid or solid. This leads to an increase "band width" due to intermolecular interactions. This means that one could have several overlapping bands in an i.r. spectrum and not be able to resolve them effectively. Matrix isolation of the sample can be used to overcome these problems. Basically, one mixes the sample under study with a large excess of an inert gas, in the gas phase, and then co-condenses them into a CsI window maintained at  $10^{\circ}\text{K}$  by a refrigeration unit. The i.r. spectrum of the material deposited on the window normally shows very sharp bands since the interaction between the inert gas and the molecule under study is minimal. Also, rotational broadening is insignificant. One observes what approximates to a gas phase spectrum with a very narrow natural line width (typically one wavenumber at half height).

This technique has one particular disadvantage when one is attempting to assign fundamental vibrations to observed bands namely matrix splitting. This may lead to the appearance of several closely spaced bands where only one would be expected. Furthermore, these splittings are dependent on the matrix used and on such factors as the rate of cooling of the matrix. The effect arises by virtue of the fact that when the matrix gas is condensed onto the cold window it can form different solid structures and so leave different types of holes for the sample molecules to occupy. For instance, the sample could occupy an octahedral or a tetrahedral hole in the matrix. This leads to a slightly different interaction between the matrix and the sample and is reflected in different frequencies for a particular vibration of the molecule under study. The difference is usually only a few wave numbers.

Fortunately this problem can be overcome by such techniques as

annealing and using several matrix gases. In the experiments discussed here, matrix effects are not important since assignments to particular vibrations of a molecule are not important. One only has to assign a band to a particular molecule.

EXPERIMENTAL

Spectra were recorded on a Perkin-Elmer 925 Spectrometer and the CsI window was maintained at 10°K by an Air Products cryostat. The CsI window was encased in a brass assembly maintained at a high vacuum ( $\sim 10^{-5}$  mm of Hg) and connected to a standard vacuum line. The brass assembly was held in the spectrometer to allow i.r. spectra to be recorded. Mixtures of gases were made up using standard manometric techniques using high purity inert gases.

Experiment A3.1

A mixture of  $H_6$ -disilyl selenide and argon in the ratio of 1 to 1000 was made up and condensed onto a CsI window held at  $10^\circ K$ . The resulting i.r. spectrum of this sample in the range  $1000-350\text{ cm}^{-1}$  is shown on figure A3.1 and some of the data obtained on table A3.1(a)

(Note: This data was taken from expanded spectra)

Experiment A3.2

A mixture of  $D_6$ -disilyl selenide and argon in the ratio of 1 to 1000 was made up and condensed onto a CsI window as before. The resulting i.r. spectrum in the range  $1000-350\text{ cm}^{-1}$  is shown on figure A3.2 and some of the data obtained on table A3.1(b)

Experiment A3.3

Equal amounts of  $H_6$ -disilyl selenide and  $D_6$ -disilyl selenide (0.5m moles each) were allowed to mix for a few minutes at room temperature in the liquid phase, in an ampoule fitted with a greaseless tap, and then mixed with argon in the ratio 1 to 1000 as before. The resulting i.r. spectrum in the range  $1000\text{ to }350\text{ cm}^{-1}$  is shown on figure A3.3 and some of the data obtained on table A3.1(c)

FIGURE A3.1

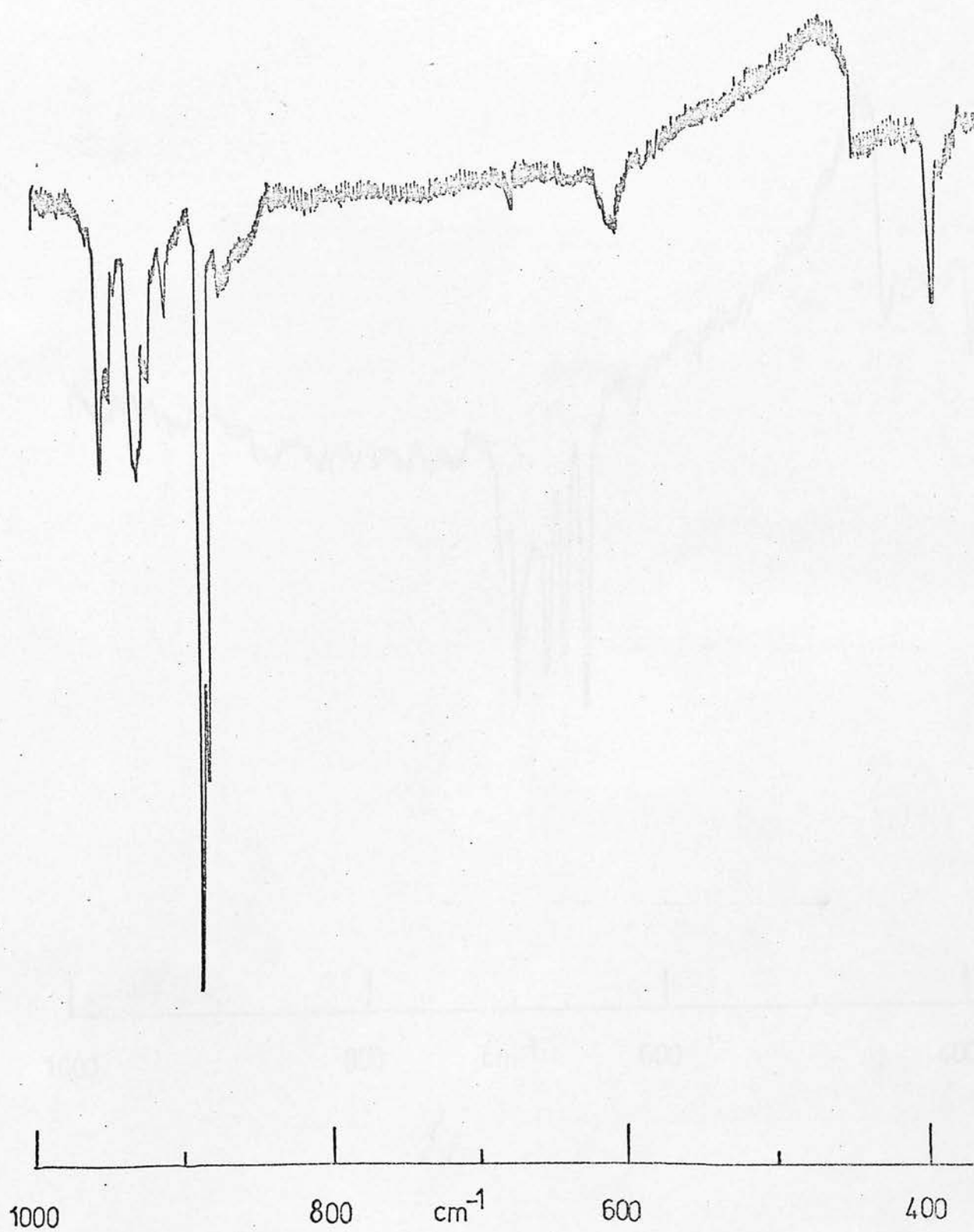




FIGURE A3.2

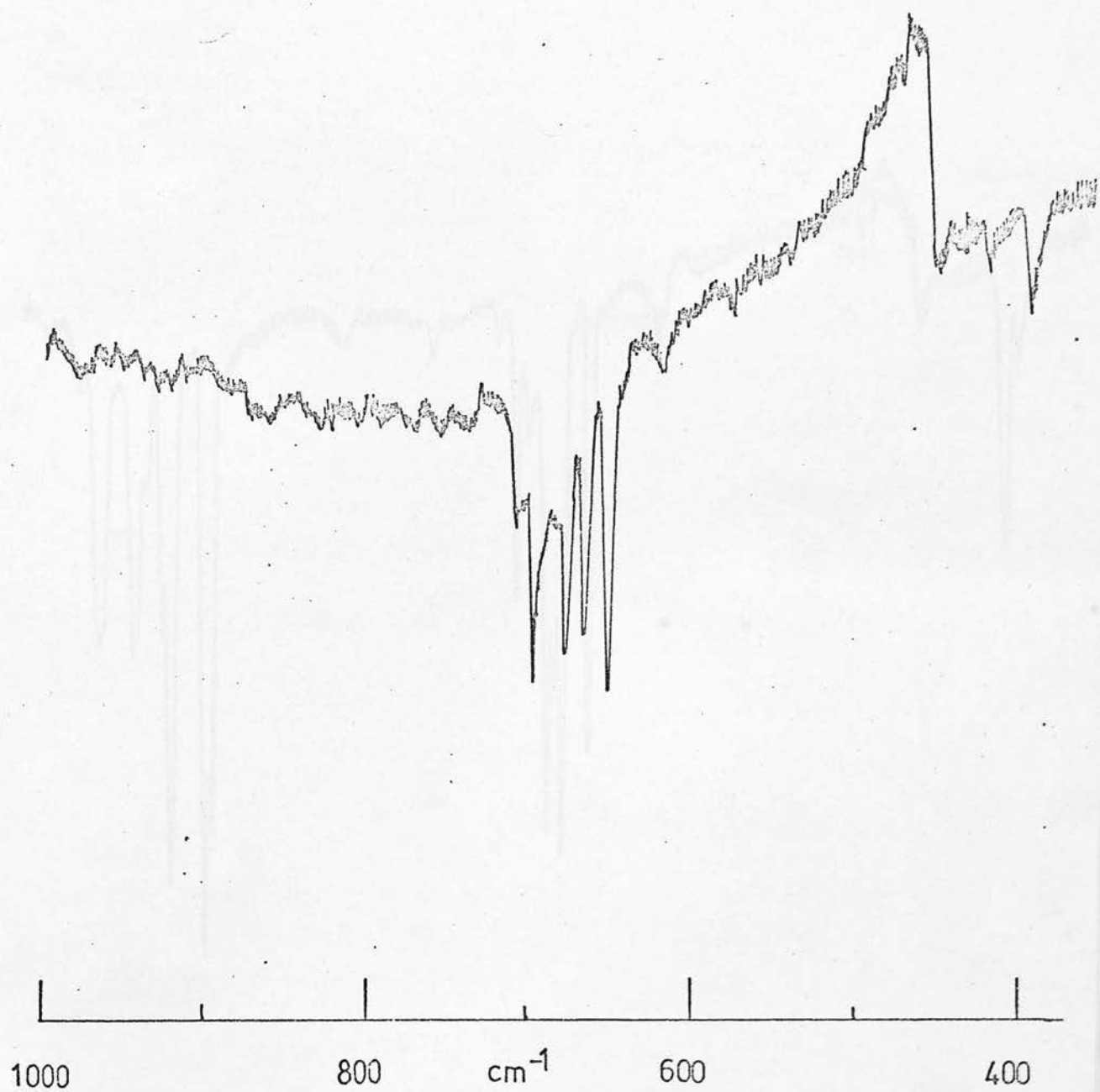


FIGURE A3.3

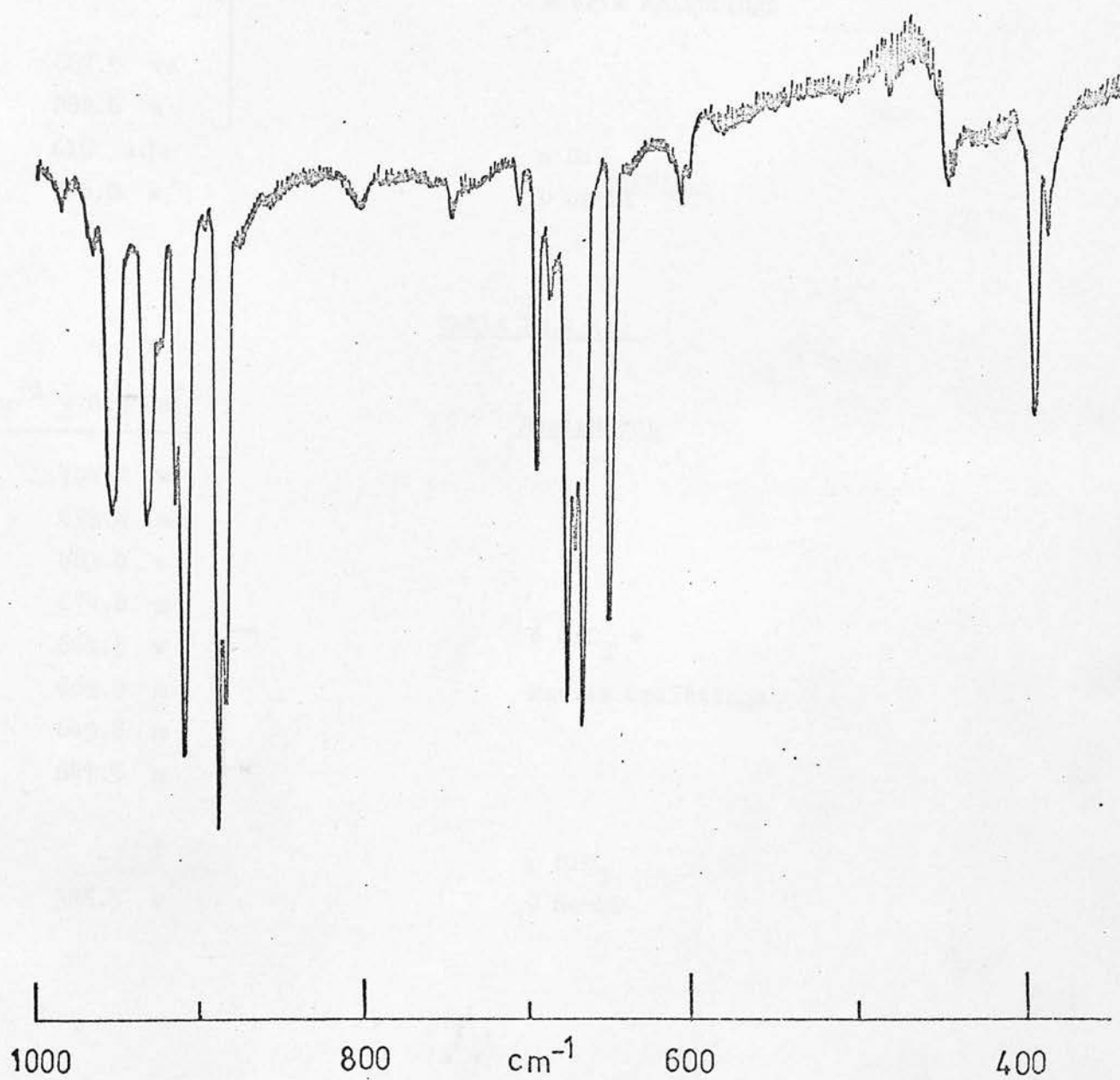


Table A3.1 (a)

<u>cm<sup>-1</sup> ± 0.5 cm<sup>-1</sup></u>	<u>Assignment</u>
954.1 m	$\delta$ SiH <sub>3</sub> + Matrix splittings
948.5 m	
933.9 vw	
931.2 m	
929.7 m	
927.0 vw	
923.6 vw	
887.0 vs	$\rho$ SiH <sub>3</sub> v Se-Si
882.6 s	
610 w.br	
396.0 m	

Table A3.1 (b)

<u>cm<sup>-1</sup> ± 0.5 cm<sup>-1</sup></u>	<u>Assignment</u>
704.2 w	$\delta$ SiD <sub>3</sub> + Matrix Splittings
693.8 m	
683.0 w	
674.8 m	
664.5 w	
663.0 m	
649.8 m	
647.5 m	$\rho$ SiD <sub>3</sub> v Se-Si
-	
386.5 w	

Table A3.1 (c)

 $\text{cm}^{-1} \pm 0.5 \text{ cm}^{-1}$ Assignment

953.5 m

951.0 m

948.0 m

933.9 m

931.0 m

927.5 m

923.5 vw

913.5 m

907.0 s

905.5 s

886.2 vs

882.5 s

 $\delta \text{SiH}_3 +$ 

Matrix Splittings

704.5 w

694.0 m

674.5 m

670.0 m

667.0 m

663.5 m

650.0 m

647.5 m

 $\delta \text{SiD}_3 +$ 

MATRIX SPLITTINGS.

610 w,br

 $\rho \text{SiH}_3$  $\rho \text{SiD}_3$ 

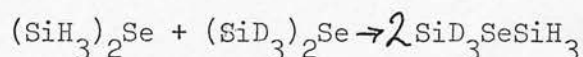
396.0 m

886.5 w

 $\nu \text{Se-Si}$

## DISCUSSION

Experiments A3.1 and 2 led to matrix isolated spectra of  $H_6$  and  $D_6$ -disilyl selenide. The frequencies of the resulting bands were measured to a high degree of accuracy ( $\pm 0.5 \text{ cm}^{-1}$ ). Experiment A3.3 showed that when equal amounts of  $H_6$  and  $D_6$ -disilyl selenide are allowed to mix at room temperature in the liquid phase then the resulting matrix isolated i.r. spectrum was not a superimposition of  $H_6$  and  $D_6$ -disilyl selenide. This can only mean that a new species is formed;  $H_3D_3$ -disilyl selenide is the only viable possibility arising from the reaction



It is difficult to assign bands to particular vibrations in the light of matrix splittings but the bands at 931.0, 913.5, 907.0, 905.5, 670.0 and  $667 \text{ cm}^{-1}$  almost certainly belong to  $H_3$ ,  $D_3$ -disilyl selenide. The bands at 907.0 and 905.5 are particularly prominent. It should be noted that none of these bands could be assigned to typical impurities such as disiloxane. The experiment was repeated and very similar results were obtained.

The reaction postulated is an exchange reaction of disilyl selenide involving Si-Se bond breakage. There is no strong thermodynamic pull on the reaction since it is an entropy driven reaction and the entropy differences involved will be very small. It is not possible to deduce that the reaction is at equilibrium but appreciable quantities of  $H_3$ ,  $D_3$ -disilyl selenide are formed within a few minutes.

It is possible to estimate a lower lifetime of a Si-Se bond in this system by using n.m.r. data. The  $^{77}\text{Se}$  satellites of disilyl selenide do not collapse at  $+70^\circ$ . This means that the lifetime of a Si-Se bond must be greater than 0.011 second at  $+70^\circ\text{C}$  and appreciably longer at room temperature.

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COURSES ATTENDED

E.S.C.A. and P.E. Spectroscopy : Dr D. Whan and Dr S. Cradock

$^{13}\text{C}$ -n.m.r. Spectroscopy : Varian Associates

n.m.r. Spectroscopy : Dr Lynden-Bell

Evening Seminars

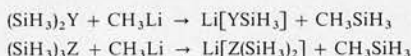
Departmental Seminars

## Lithium-Derivate von Silanol und verwandten Verbindungen

Von Stephen Cradock, E. A. V. Ebsworth, Hans Moretto, David W. H. Rankin und W. John Savage<sup>[\*]</sup>

Während Disilylphosphan sich bei geringem Druck noch als relativ stabil erweist, gilt dies nicht für Silanthiol sowie Silanselenol; Silanol ist bisher nicht bekannt<sup>[1]</sup>. Eine direkte Synthese von Alkalimetall-Derivaten dieser Verbindungen erscheint daher wenig aussichtsreich.

Wir haben gefunden, daß sich Methyllithium in Diäthyläther bei 227 °K in wenigen Minuten glatt mit Silylverbindungen des Typs  $(\text{SiH}_3)_2\text{Y}$  ( $\text{Y} = \text{O}, \text{S}, \text{Se}$ )<sup>[2]</sup> oder  $(\text{SiH}_3)_3\text{Z}$  ( $\text{Z} = \text{P}, \text{As}$ ) umsetzt. Ungefähr 90% des nach



entstehenden Methylsilans wird dabei freigesetzt. Die entsprechenden Lithium-Derivate lassen sich nach Abziehen des Lösungsmittels unter vermindertem Druck als farblose, kristalline Feststoffe isolieren. Sie wurden anhand ihrer Raman-Spektren (fest oder in Lösung; vgl. Tabelle 1 und 2) charakterisiert.

Tabelle 1. Raman-Spektren ( $\text{cm}^{-1}$ ) von Lithium-silanthiolat und -silanselenolat  $\text{Li}[\text{YSiH}_3]$  in Diäthyläther.

$\text{Y} = \text{S}$	$\text{Y} = \text{Se}$	Zuordnung
2130 m, p	2118 m, p	$\nu_s \text{SiH}$
945 s(br), dp	940 s(br), dp	$\delta \text{SiH}_3$
655 ss(br), dp	624 ss(br), dp	$\rho \text{SiH}_3$
565 st, p	429 sst, p	$\nu \text{SiY}$

Tabelle 2. Raman-Spektren ( $\text{cm}^{-1}$ ) von Lithium-disilylphosphid und -disilylarsenid  $\text{Li}[\text{Z}(\text{SiH}_3)_2]$  in Diäthyläther.

$\text{Z} = \text{P}$	$\text{Z} = \text{As}$	Zuordnung
2105 m, p	2110 m, p	$\nu_s \text{SiH}$
940 s(br), dp	930 m(br), dp	$\delta \text{SiH}_3$
635 ss(br), dp	580 s(br), dp	$\rho \text{SiH}_3$
495 m, dp	—	$\nu_{\text{as}} \text{Si}_2\text{Z}$
470 st, p	374 sst, p	$\nu_s \text{Si}_2\text{Z}$
145 s, p?	122 s, p?	$\delta \text{Si}_2\text{Z}$

Die  $^1\text{H}$ -NMR-Spektren dieser Verbindungen zeigen im allgemeinen das erwartete  $\text{SiH}$ -Singulett mit Satelliten, die auf  $^{29}\text{Si}$  natürlicher Häufigkeit zurückzuführen sind [ $^1\text{J}(^{29}\text{SiH}) \approx 200 \text{ Hz}$ ]. Unter heteronuclearer Entkopplung findet man bei  $\text{Li}[\text{YSiH}_3]$  das  $^{29}\text{Si}$ -Spektrum wie zu erwar-

ten als Quartett scharfer Linien, während das  $^{29}\text{Si}$ -Spektrum bei  $\text{Li}[\text{Z}(\text{SiH}_3)_2]$  aus einem Quartett von Quartetts [ $^3\text{J}(^{29}\text{SiH})!$ ] besteht. Im Falle  $\text{Z} = \text{P}$  erscheint die  $\text{SiH}$ -Hauptresonanz bei Raumtemperatur als Dublett [ $^2\text{J}(^{31}\text{PH}) = 15.5 \text{ Hz}$ ], und heteronucleare Entkopplung ergibt das  $^{31}\text{P}$ -Spektrum als Heptett. Im Falle  $\text{Y} = \text{Se}$  erscheinen bei tiefer Temperatur durch  $^{77}\text{Se}$  hervorgerufene Satellitensignale [ $^2\text{J}(^{77}\text{SeH}) = 11 \text{ Hz}$ ]; sie kollabieren oberhalb 273 °K vermutlich aufgrund eines Austauschprozesses. Bei 253 °K läßt sich das  $^{77}\text{Se}$ -Spektrum als Quartett beobachten.

$\text{LiSSiH}_3$  sowie  $\text{LiSeSiH}_3$  reagieren in Lösung mit Trimethylchlorsilan zum Disilathian  $\text{H}_3\text{Si}-\text{S}-\text{Si}(\text{CH}_3)_3$  bzw. Disilasesenan  $\text{H}_3\text{Si}-\text{Se}-\text{Si}(\text{CH}_3)_3$ , die durch ihre Schwingungsspektren charakterisiert wurden. Wir untersuchen zur Zeit das Leistungsvermögen der neuen Lithiumsalze für weitere Synthesen.

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